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UNIVERSITY OF ALBERTA

THERMOLYSIS OF 3,5-DIMETHYL-4-METHYLENE-1-PYRAZOLINES

BY

JOHN HIEBERT

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF

DOCTOR OF PHILOSOPHY ©

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
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FACULTY OF GRADUATE STUDIES AND RESEARCH

THE UNDERSIGNED CERTIFY THAT THEY HAVE READ, AND RECOMMEND TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH FOR ACCEPTANCE, A THESIS ENTITLED Thermolysis of 3,5-Dimethyl-4-methylene-1-pyrazolines SUBMITTED BY JOHN HIEBERT IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy.

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Date: January 15 1991

ABSTRACT

The gas phase thermolyses of *cis* and *trans*-3,5-dimethyl-4-methylene-1-pyrazoline at 170°C proceeded at a rate consistent with previous 4-alkylidene-1-pyrazoline results, the thermolysis of which are believed to occur by a one-bond homolysis mechanism.

The thermolysis of a 93.4 ± 2.0% ee sample of chiral (-)-*trans*-3,5-dimethyl-4-methylene-1-pyrazoline containing 4.1 ± 0.2% *cis*-3,5-dimethyl-4-methylene-1-pyrazoline produced alkylidenecyclopropane products with no observable optical rotation. Limitations of optical detectability were estimated at <2.0% of *trans*-2,3-dimethylmethylenecyclopropane, <5.0% of E-2-methylethylidenecyclopropane, and <10% Z-2-methylethylidenecyclopropane from an enantiomerically and diastereomerically pure chiral *trans*-3,5-dimethyl-4-methylene-1-pyrazoline. The enantiomeric purity of the optically active sample of (-)-*trans*-3,5-dimethyl-4-methylene-1-pyrazoline was obtained by using ^{1}H-NMR techniques involving lanthanide shift reagents with the pyrazolines synthetic precursor (+)-*trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione. Synthetic steps generating the chiral pyrazoline did not lead to any loss of optical activity.

These results eliminate the possibility of product methylenecyclopropanes being formed from diazenyl radical intermediates. The results are best rationalized in terms of products formed from a partial equilibrium of orthogonal Chesick diradical and planar trimethylenemethane intermediates with the Chesick diradicals possibly being formed by nitrogen loss from rotamer equilibrated diazenyl radical intermediates.

The thermolysis of 98.1% *cis* and >99.8% *trans*-3,5-dimethyl-4-methylene-1-pyrazoline at 170°C produced *trans*-2,3-dimethylmethylenecyclopropane, *cis*-2,3-dimethylmethylenecyclopropane, E-2-methylethylidenecyclopropane, and Z-2-methylethylidenecyclopropane in a ratio of 15.8 : 42.8 : 33.4 : 7.8 and 15.9 : 12.0 : 59.4 : 12.7 respectively. The *cis* and *trans* pyrazoline stereochemical assignments were made on the basis of the X-ray structure of *trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione.

Implications of the above results are discussed.

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The author wishes to thank the staff of the spectroscopy laboratories for their valuable contributions and the technical staff for their support.

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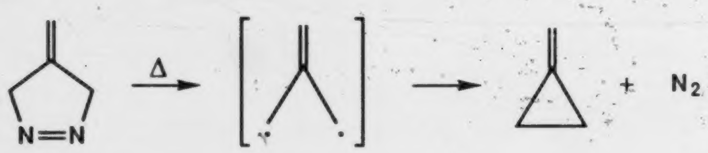
INTRODUCTION

The determination of the thermolysis mechanism of linear and cyclic azoalkanes has held the interest of scientists for a minimum of four decades and is still the subject of investigation[1-6] and speculation[7-9]. 4-Alkylidene-1-pyrazolines, the subject of this research, comprise a class of cyclic azoalkanes that also has a thermolysis mechanism(s) that is difficult to ascertain.

Carbon-Nitrogen Bond Cleavage

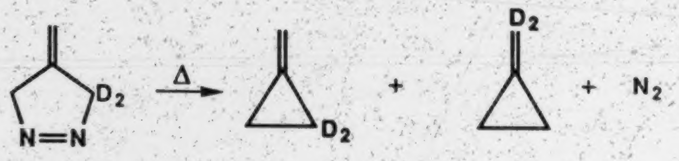
The formation of methylenecyclopropane **3** and nitrogen gas from the parent 4-methylene-1-pyrazoline **1** (Eq. 1) suggests that both C-N bonds are homolitically broken to yield a diradical intermediate such as **2** which then forms product by bond formation between the two radical centers. This simple mechanism is readily discredited by the results in Eq. 2 where deuterium substitution of the parent 4-alkylidene-1-pyrazoline leads to the formation of two products. A more complex mechanism involving stereochemical features is obviously occurring.



1 **2** **3**

(Eq. 1)

Numerous studies have been directed towards understanding the initial C-N bond cleavage and in understanding the factors governing product formation with regard to 4-alkylidene-1-pyrazolines. It has been



4 5 6

(Eq. 2)

difficult to determine whether both carbon-nitrogen bonds are homolytically broken (Eq. 3) in the initial rate determining step, or whether a non-concerted stepwise homolytic carbon-nitrogen breakage occurs (Eq. 4) yielding a reactive diazenyl radical intermediate. A comparison of the activation energies of the azoalkanes **1,15,7-12** in Table 1 indicates a stepwise cleavage of C-N bonds for both acyclic azoalkanes and for 4-alkylidene-1-pyrazolines. An approximate 10 kcal/mole decrease in the

$$\text{R-N=N-R}' \rightarrow \text{R}\cdot \ \ \text{N}_2 \ \ \cdot\text{R}'$$

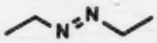
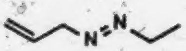
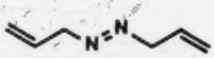
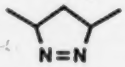
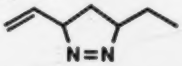
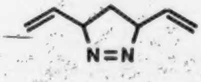
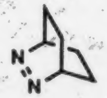
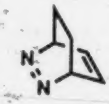
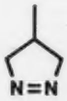
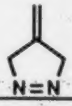
(Eq. 3)

$$\text{R-N=N-R}' \rightarrow \text{R-N=N}\cdot \ \ \cdot\text{R}'$$

(Eq. 4)

activation energy of compound **8** and **11** relative to compound **7** and **10** respectively is consistent with a possible resonance stabilization of a breaking allylic C-N bond; however placing an α–allyl group next to each C-N bond as in **9** or **1** does not yield a further net decrease in the activation energy as one might expect if two breaking C-N bonds were stabilized. In contrast, for the cyclic 1-pyrazolines (compounds **10-12** in Table 1), there is an approximate 10 kcal/mole decrease in activation energy for each C-N bond that is made allylic. Thus both radical centres are stabilized through

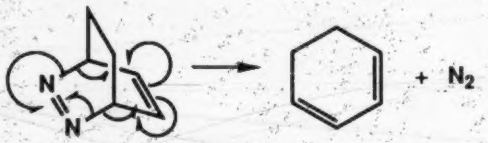
Table 1 Activation parameters for some selected azo compounds[45]

	Compound	Cond.[a]		E_a. (kcal/mol)	log A.	Ref.
7		g		47.7	15.4	10
		f		45.7	14.6	
8		g		35.6 ± 0.5	14.8 ± 0.3	11
9		g		36.1 ± 0.2	15.5 ± 0.2	12
10		g	*cis*	40.5 ± 0.4	15.5 ± 0.2	13
		g	*trans*	40.3 ± 0.4	15.6 ± 0.2	13
11		Ph_2O	*cis*	31.3 ± 0.3	14.3± 0.3	14
12		Ph_2O	*cis*	22.9 ± 0.5	12.8 ± 0.3	14
			trans	25.8 ± 0.4	14.0 ± 0.3	14
13		g		44.5 ± 0.1	15.3 ± 0.1	15
14		-78° Sol'n		< 14		16
15		g		42.3 ±0.3	15.8 ±0.3	13
1		g		32.6 ±0.3	13.24	17

[a] g - gas phase, f - flow system

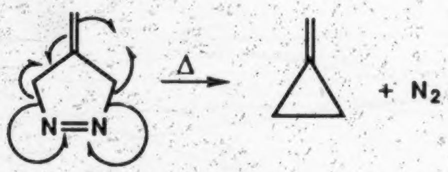
resonance in the rate determining step. A process which is consistent with simultaneous cleavage of both bonds as shown in (Eq. 3).

Unsaturation placed in a compound in such a way that a symmetry allowed electrocyclic process is possible, such as in compound **14** in Table 1 (Eq.5), leads to a much larger decrease in activation energy (>30 kcal/mole) than is exhibited by the other two series of compounds. This type of process is geometrically more difficult for 4-alkylidene-1-pyrazolines[18] (Eq. 6). and is therefore a less probable mechanism.



14 **16**

(Eq. 5)



1 **3**

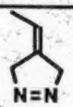
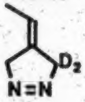
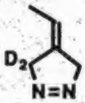
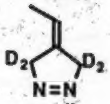
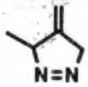
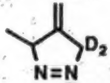
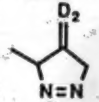
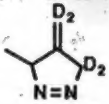
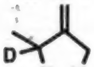
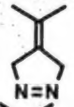
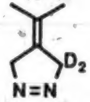
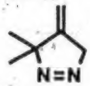
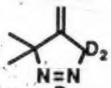
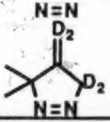
(Eq. 6)

It has been suggested by Engel[19] that acyclic azoalkanes follow a continuum of mechanisms between (Eq. 3) and (Eq. 4), with unsymmetrical azo compounds biased towards stepwise cleavage. More recent evidence in terms of "turnaround" solution cage products[20] and pressure dependent solution phase thermolysis rates[2] supports a stepwise mechanism for unsymmetrical acyclic azoalkanes while molecular orbital calculations indicate that this may also be the case for symmetrical compounds[21,22].

Our laboratory has compiled kinetic isotope effects (KIE) for a large number of 4-alkylidene-1-pyrazolines (Table 2)[18,5]. The magnitude of the KIE (k_H/k_D) varies between 1.02 for compound **25** and 1.29 for compound **20** which is consistent with an α-secondary isotope effect resulting from the breakage of a C-N bond in the rate determining step. The variation of KIE magnitudes is consistent with a single C-N bond homolysis mechanism in which there is a preferential cleavage of the two possible C-N bonds. The largest KIE is observed for 3,3,5,5-tetradeutero-4-ethylidene-1-pyrazoline **20** since a KIE would be observed for 100% of all reactions occurring. For compounds in which only the C_3 or C_5 position is deuterated, a smaller KIE is expected, and is observed, for one-bond cleavage since only a fraction of total reactions would result in a KIE.

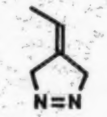
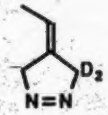
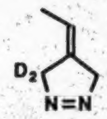
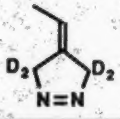
The variation in KIE is also possible in a concerted but unsymmetrical cleavage of both C-N bonds. The magnitude of the KIE for the C_3 or C_5 deuterated 4-alkylidene-1-pyrazolines would then be dependent on the extent of bond breakage in the transition state. Thus, on the basis of KIE alone, an algebraic differentiation between the two mechanisms is not possible and the energetics of such processes must be evaluated. Table 3[18] contains values for $\delta\Delta G^{\ddagger}/n$ (Eq. 7) calculated from k_H/k_D values recorded in Table 2 for both one-bond (scheme 1) and two-bond (scheme 2) homolysis mechanisms. For the one-bond cleavage mechanism, partitioning between the two C-N bonds is calculated on the assumption that k_H/k_D is constant for both α and β cleavages. The large 30-78 cal/mole range for $\delta\Delta G^{\ddagger}/n$ for two-bond cleavage is clearly outside the 90-120 cal/mole/D range that generally characterizes[23] significant C-N

Table 2 Secondary deuterium kinetic isotope effects for some 4-methylene-1-pyrazoline derivitives[5]

Compound		Temp (°C)	10^3k (s^{-1})	$(k_H/k_D)^{corr}$	δΔG‡ (cal/mol)	Ref
17		164.0 ± 0.1	1.94 ± 0.01			18
18		•	1.63 ± 0.02	1.19 ± 0.03[a]	157	18
19		•	1.82 ± 0.02	1.07 ± 0.02	59	18
20		•	1.51 ± 0.02	1.29 ± 0.03	221	18
21		180.0 ± 0.1	3.01 ± 0.03			5
22		•	2.55 ± 0.05	1.18 ± 0.03	149 ± 20	5
23		•	2.86 ± 0.05	1.05 ± 0.02		5
24		•	2.52 ± 0.02	1.19 ± 0.02	157 ± 20	5
25		•	2.94 ± 0.02	1.02 ± 0.02	17 ± 17	5
26		•	1.75 ± 0.02			5
27		•	1.57 ± 0.01	1.12 ± 0.02	102 ± 16	5
28		•	2.14 ± 0.01			5
29		•	1.83 ± 0.02	1.18 ± 0.03	149 ± 20	5
30		•	1.79 ± 0.05	1.20 ± 0.03	164 ± 20	5

[a] Corrected for incomplete deuteration

Table 3 The ratio of k_α:k_β for one-bond cleavage of deuterated 4-ethylene-1-pyrazolines, and of $\delta\Delta G^‡/n$ calculated for one-bond and two-bond cleavage mechanisms [18]

Reactant		k_α:k_β	$\delta\Delta G^‡/n$ (cal/mole)[a] one-bond cleavage	$\delta\Delta G^‡/n$ (cal/mole)[a] two-bond cleavage
17		72:28		
18		67:33	110 ± 4	78 ± 3
19		77:23	110 ± 4	30 ± 2
20		72:28	110 ± 4	57 ± 2

[a] calculated from (Eq. 7)

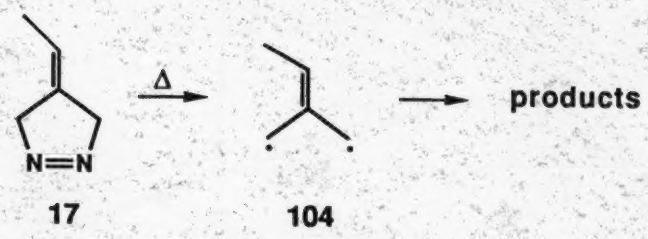
$$\delta\Delta G = (RT/n)\ln(k_H/k_D)$$

n = number of deuteriums on the α-carbon undergoing valence change in the rate determining step.

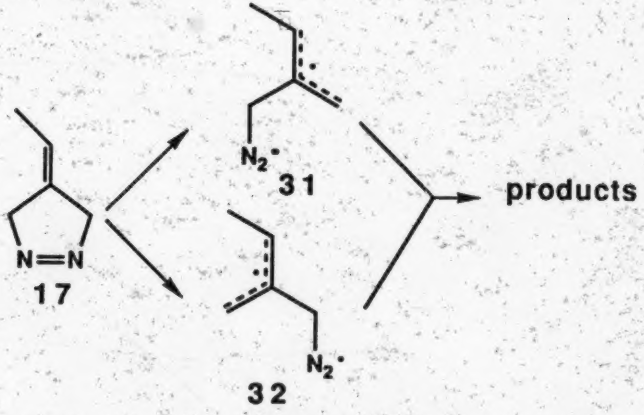
(Eq. 7)

bond cleavage in the rate determining step. The 110 cal/mole/D for one-bond cleavage, however, is consistent with the expected values.

The $\delta\Delta G^‡/n$ values for compounds **33-36** (Table 4) however, give an ambiguous result. The deuterated 4-methylene-1-pyrazolines give $\delta\Delta G^‡/n$ values of 60-70 cal/mole and ~142 cal/mole for one-bond and two-bond cleavages respectively, neither of which falls in the characteristic[23]



Scheme 1

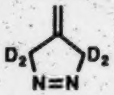
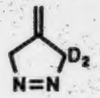
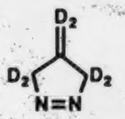
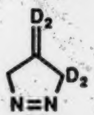
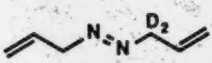
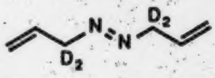


Scheme 2

90-120 cal/mole range. It should be noted, however, that the diallyl azo compounds **37** and **38** provide compelling evidence favouring single C-N bond cleavage[12] and yield very similar results for the two pathways. Their relatively large KIE may be indicative of complete C-N bond rupture in the rate determining step.

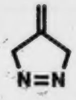
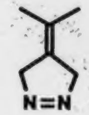
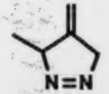
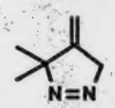
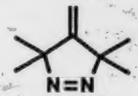
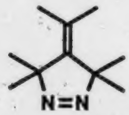
The radical producing thermolysis of linear azoalkanes (R-N=N-R) follows the general rule[19] that C-N homolysis rates are dependent on the

Table 4 Values of $\delta\Delta G^{\ddagger}/n$ calculated for one-bond and two-bond cleavage mechanisms of selected 4-methylene-1-pyrazolines

	Reactant	k_H/k_D	$\delta\Delta G^{\ddagger}/n$ (cal/mole)		Ref
			two-bond	one-bond	
33		1.38 ± 0.02	71 ± 3	142 ± 6	24
34		1.15 ± 0.01	62 ± 5	142 ± 12	24
35		1.42 ± 0.02	71 ± 3	141 ± 6	24
36		1.19 ± 0.01	64 ± 4	142 ± 9	24
37			66 ± 10	135 ± 15	12
38			66 ± 10	135 ± 15	12

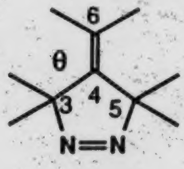
degree of alkyl substitution on the carbon *alpha* to the nitrogen, that is 3°>2°>1°. The incipient stability of the resulting intermediate radical (1-2 kcal/mole per methyl) is usually considered the driving force for this trend. The thermolysis of 4-alkylidene-1-pyrazolines (Table 5), however, produces unusual relative rates and enthalpy changes when methyl groups replace hydrogen[18,17,25,26]. Substitution *alpha* to the nitrogen leads to little effect as in the mono-substituted **21**, or to a significant decrease as in the gem-dimethyl substituted **28** or tetramethyl substituted **39**. Substitution on the exocyclic methylene leads to a decrease in rate as in compound **26**.

Table 5 Activation parameters and relative rates at 170°C for some 4-alkylidene-1-pyrazolines[5]

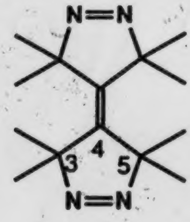
	Compound	E_a.(kcal/mole)	log A	rel. rate at 170°C	Ref.
1		33.6 ± 0.7	13.75 ± 0.35	1.00	17
26		35.9 ± 1.0	14.6 ± 0.9	0.55	18
21		33.0 ± 1.0	13.4 ± 1.0	1.04	18
28		35.3 ± 1.2	14.4 ± 0.6	0.70	18
39		40.7 ± 0.4	15.5 ± 0.2	0.020	26
40		39.8 ± 0.4	13.6 ± 0.4	0.00065	25

Major decreases in rate occur when both the exocyclic methylene and α-carbons are methyl-substituted as in **40**.

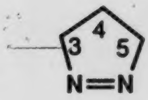
The X-ray structure for permethyl-4,4-bis-($\Delta^{1,2}$-pyrazolinylidene) **42** by Bushby and Pollard [27] shows the $C_3C_4C_5$ bond angle to be 103.8°. The $C_3C_4C_5$ bond angle for 1-pyrazoline **43** has also been determined[28] as 99.1°. Thus one would expect that bond homolysis for 4-alkylidene-1-pyrazolines would release ground state strain, particularly when methyl substitution leads to increased steric effects. LeFevre and Crawford[5] have attributed the anomalous decrease in rate for compounds **26** and **40** relative to **1** and **39**, to steric crowding in the transition state resulting from a decrease in the $C_3C_4C_6$ bond angle (θ) during homolysis of a C-N bond (see **41**).



41



42

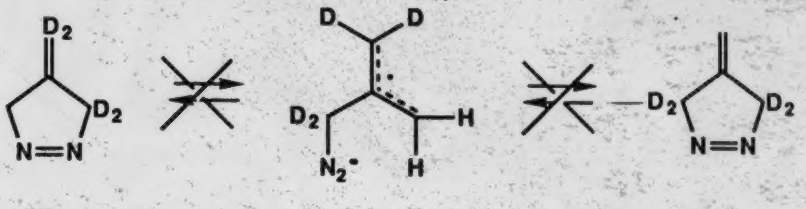


43

KIE and free energies of activation were interpreted by Crawford *et al.* [18,5,17] as indicating the extent of steric compression in the transition state. A comparison of **18** and **19**, **22** and **25** (Table 2) clearly indicates that the C-N bond anti to the exocyclic ethylidene or opposite to an α-methyl has a larger KIE. In terms of a one-bond homolysis mechanism, a larger KIE indicates a preference for cleavage of the C-N bond which is consistent with the proposed transition state compression theory. It was also noted that $\delta\Delta G^{\ddagger}/n$ for **29** equals 75 ± 10 kcal/mole per deuterium (calculated for one-bond cleavage), which is only slightly less than the 90-120 kcal/mole expected[23] for complete C-N bond rupture. Thus compounds with large KIE such as **29**, **22** and **18** cleave primarily the C-N bond opposite or anti to methyl substitution.

An aspect of the rate determining homolytic C-N cleavage assumed and critical in the prior analysis is its irreversibility. A control run[29] of **36** (Eq. 8) quenched at 50% completion and then re-isolated indicated no observable increase of deuterium in the allylic position, i.e., no formation of **33**. It was estimated that a 2% rearrangement could have been detected;

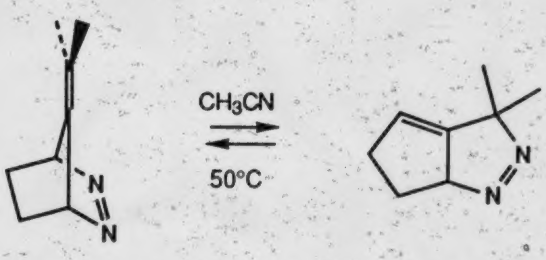
therefore, reversibility of one-bond homolysis is unlikely. Reversibility for α-methylated 4-alkylidene-1-pyrazolines is improbable since the lifetime of a diazenyl radical should be shorter due to the increased stability of the alkyl radical.



36 44 33

(Eq. 8)

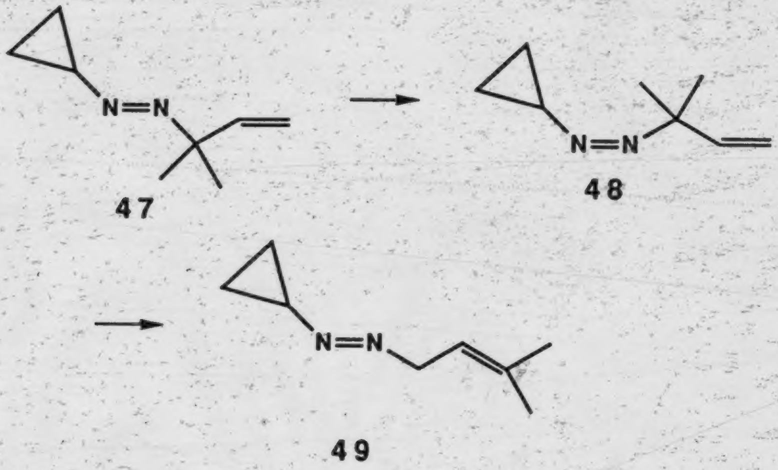
Other researchers have shown that reversibility of azoalkanes is possible; however, special circumstances are involved. Berson[20,31] observed rearrangement in the thermolysis of the bicyclic **45** to form **46** (Eq. 9). It has been suggested, though, that the geometry of the bicyclic ring system allows an easier access to C-N bond formation by an intermediate diazenyl radical.



45 46

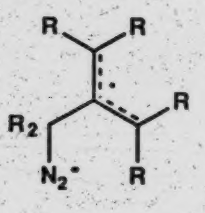
(Eq. 9)

Engel and Gerth[20] have observed reversibility of linear azoalkanes (Eq. 10). Irradiation at 25°C of *trans* **47** produces the thermally labile *cis* **48**, which, besides producing the expected hydrocarbons, produces the "turnaround" azoalkane **49**. They have noted that the amount of "turnaround" product decreases with the increasing stability of R· from the intermediate R-N=N·, indicating a competition between β-scission of R-N=N· and recombination. The recombination, however, is a cage phenomenon resulting from the reaction being performed in solution.

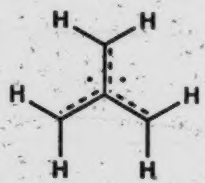


(Eq. 10)

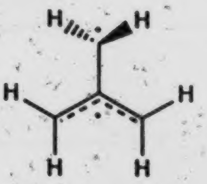
In summary, the majority of the evidence available suggests that the first step of 4-alkylidene-1-pyrazoline thermolysis is an irreversible rate determining one C-N bond homolysis that is very sensitive to steric factors resulting in unusual decreases in rate with methyl substitution. This mechanism produces the diazenyl radical intermediate **50**. Problems with this generalization do arise, however, with regard to deuterated 4-alkylidene-1-pyrazolines (see Table 3).



50



51

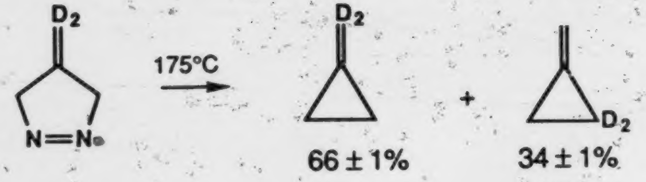


52

Product Determining Step

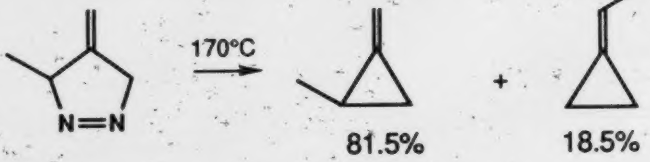
Equations 11-16 rule out product formation resulting from the original 4-alkylidene-1-pyrazoline carbons *alpha* to the nitrogens becoming exclusively the alkylidenecyclopropane ring carbons, i.e., only one product should be formed. Thus, a fully concerted mechanism, or a mechanism resulting in an intermediate diradical (with no allylic radical scrambling) and subsequent alkylidenecyclopropane formation (Eq. 1) are unlikely. Crawford *et al.*[29] suggested that only one product may be formed from a concerted process in the gas phase; however, the alkylidenecyclopropane was "hot" leading to isomerization and thus formation of other 4-alkylidenecyclopropanes. They discovered, though, that **55** (Eq. 14) which should be the first product formed from 3,3-dideutero-4-methylene-1-pyrazoline **34** was present in 59 ± 1%. The equilibrium value for **55** was determined at 67.6%. This would have required the impossible, i.e., isomerization had exceeded the equilibrium value. The observation that the same product ratios were obtained in solution further discredited the "hot species" argument.

A sequential or concerted homolysis of both C-N bonds to form a planar trimethylenemethane (TMM) with D_{3h} symmetry **51** can also be ruled out[17] since **53** and **34** (Eq. 11,14), **21**and **17** (Eq. 12,15), and **28** ref



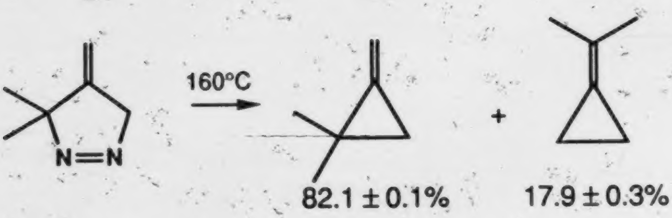
17

53 **54** **55** (Eq. 11)



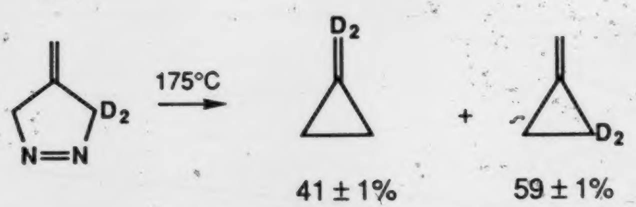
5

21 **56** **57** (Eq. 12)



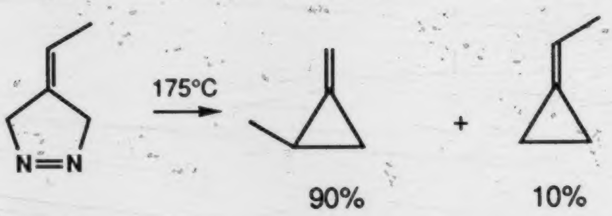
29

28 **58** **59** (Eq. 13)



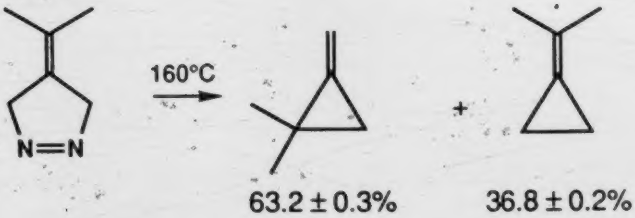
17

34 **54** **55** (Eq. 14)



18

17 **56** **57** (Eq. 15)

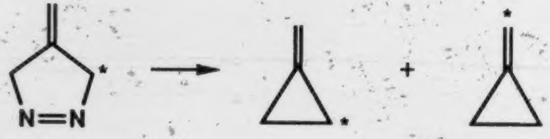


29

26 **58** **59** (Eq. 16)

and **26** (Eq. 13,16) would give common intermediates and, therefore, the same product ratios. Similarly, rapidly equilibrating orthogonal TMM **52** cannot be possible[17] since common intermediates would again be attained by the corresponding pairs of reactions (Eq. 11-16).

Crawford *et al.*[29] thermolysed a ^{13}C enriched sample of 4-methylene-1-pyrazoline (Eq. 17). They determined (Table 6) that the statistically random ratio of **61/62** = 2.00 was not obtained. Since changing the mass (^{13}C) on a rotational axis should eliminate any "ponderal" effect, they concluded that the original position of the methylene group influenced the final position of that group in the methylenecyclopropane. Thus D_{3h} symmetry intermediates (**51**) are not possible even with non-substituted 4-methylene-1-pyrazolines.

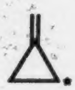
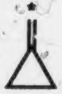


60 **61** **62**

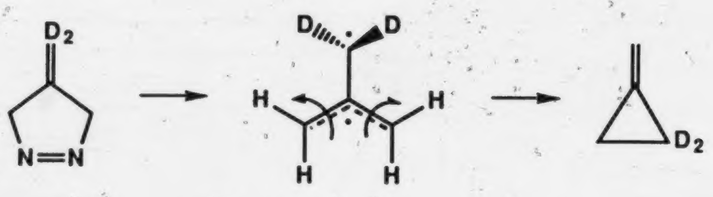
(Eq. 17)

Crawford and Chang[17] also considered the possibility that the exomethylene group of the pyrazoline rotates to form an orthogonal-TMM and then one of the allylic methylenes rotates to close the diradical (Eq. 18). This suggestion was rejected since 4-dideuteromethylene-1-pyrazoline **53** (Eq. 11) should give but one product **55**, and similarily **26** (Eq. 16) would give only **58**, and **17** (Eq. 15) would give only **56**. All three pyrazolines produce two alkylidenecyclopropanes.

Table 6 The proton integration of the ^{13}C side bands of **61** and **62** from the thermolysis of **60** (1 hour at 165°C)

Pressure (torr)	61/62[a]	% products	
		 **61**	 **62**
450	1.76 ± 0.04	63.7 ± 0.5	36.3 ± 0.5
350	1.75 ± 0.04	63.6 ± 0.5	36.4 ± 0.5
250	1.82 ± 0.04	64.5 ± 0.6	35.5 ± 0.5

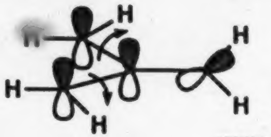
[a] Standard deviation of eight or more analyses of each sample.



53 **63** **55**

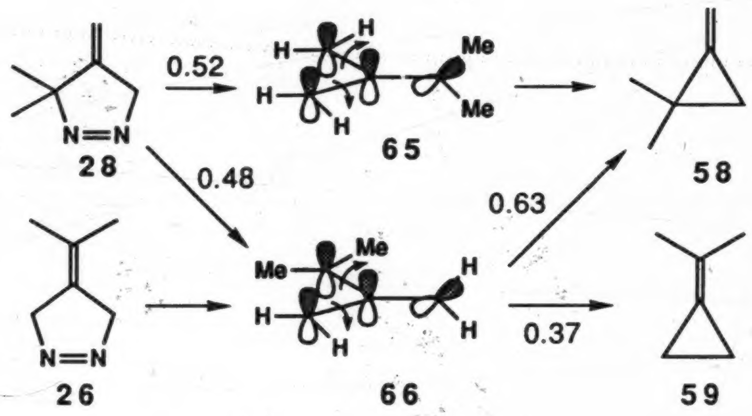
(Eq. 18)

It is also possible to create an orthogonal TMM **52** by rotating the methylene group of the breaking C-N bond (one bond homolysis) so that its semi-vacant orbital is parallel to the original olefin π orbitals. The remaining nitrogen bearing carbon then loses molecular nitrogen to form the orthogonal "p" orbital. The above process accounts for enhanced rates for 4-methylene-1-pyrazoline **1** relative to 4-methyl-1-pyrazoline **15** (Table 1) since there would be allylic resonance developing in the transition state. The orthogonal TMM **52**, also known as a Chesick diradical[32], is redrawn to display its "p" orbitals in structure **64**. On the basis of least motion principals[33] it would be expected that either one of the two coplanar methylene groups could rotate out of the plane as shown in **64**, to form a new C-C bond by overlap with the orthogonal singly-occupied orbital.



64

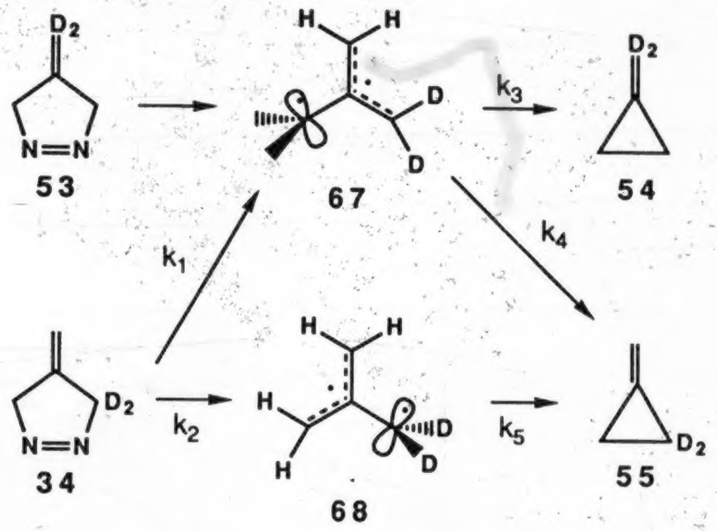
The products from the thermolysis of 3,3-dimethyl-4-methylene-1-pyrazolines **28** and 4-isopropylidene-1-pyrazoline **26** can be rationalized[29] in terms of a Chesick diradical intermediate. Scheme 3 reflects that the homolysis of either C-N bond of compound **26** gives intermediate **66** Separate rotation of either of the planar allylic alkyl groups then produces alkylidenecyclopropanes **58** and **59**. Since the two C-N bonds of **28** are non-equivalent, thermolysis may produce two intermediates. Chesick diradical **65** would generate exclusively **58** while intermediate **66** responds as described previously. Mathematically, the product proportions can be rationalized if rotation of the isopropylidene group is favoured 63:37 over that of the methylene group. The preference may be rationalized[19] in terms of the relief of strain, or the greater stability of tertiary radicals. Since **59** is thermodynamically more stable than **58**, the preference is not controlled by the stability of the products. Scheme 3 also requires that **65** and **66** be produced in the ratio of 48:52, i.e., the C-N bond opposite to the α-gem dimethyl group is preferentially broken. This result is compatible with the steric arguments presented previously (page 11).



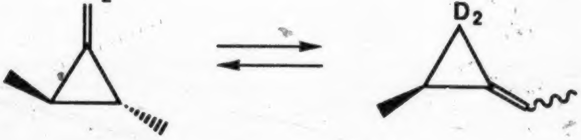
Scheme 3

Crawford's research group tried to apply[29] Chesick diradical behavior to rationalize product proportions derived from the thermolysis of 4-methylene-1-pyrazolines with primary allylic carbons such as the tetradeuterio **36** and the ^{13}C enriched **60**, however, either mathematical predictions did not match experimental results or questionable assuptions had to be made. An example of the problems that occur when trying to apply Chesick diradicals to 4-methylene-1-pyrazolines with primary allylic cabons can be seen in Scheme 4. Mathematically, solutions are available to fit the scheme and the product ratio obtained experimentally; however, the ratio k_1/k_2 which represents the second order rate KIE for the thermolysis of **34** has an impossible value of -0.17, and the ratio k_3/k_4 which is simply the ratio of products **54/55** derived from **53** has a value of 0.52 ± 0.02. This implies that rotation of the CD_2 group of **67** is twice as facile as that of the CH_2 group. Classical inertial arguments estimate k_3/k_4 to be 1.4[34,35]. Crawford and Chang[18,17] later estimated that the rate of rotation of the CH_2 group out of the planar allylic system such as **67** is 1.33

times as fast as that of the CD_2 group (R = 1.33). The legitimacy of R=1.33 ± 0.05 is substantiated by Gajewski and Chou[36] who have determined a KIE of 1.31 ± 0.05 for the thermal isomerization of methylenecyclopropane **69** to ethylidenecyclopropane **70** in (Eq. 19). This kinetic isotope effect is explained in terms of a loss of the torsional vibrational mode by an allylic $CH_2(CD_2)$ upon rotation out of the allylic plane during product formation.



Scheme 4

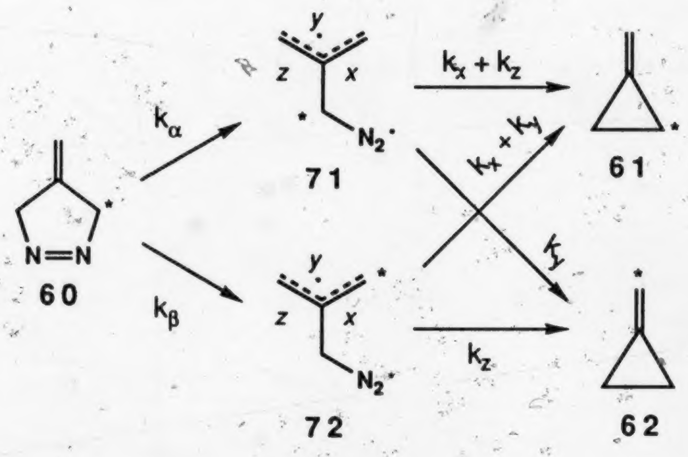


69

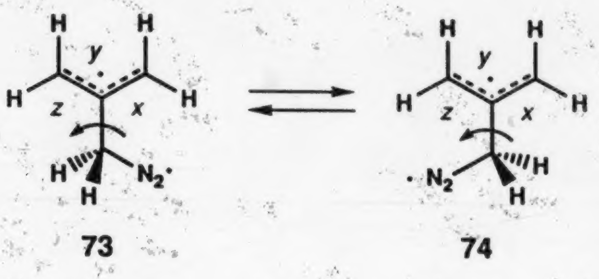
70

(Eq. 19)

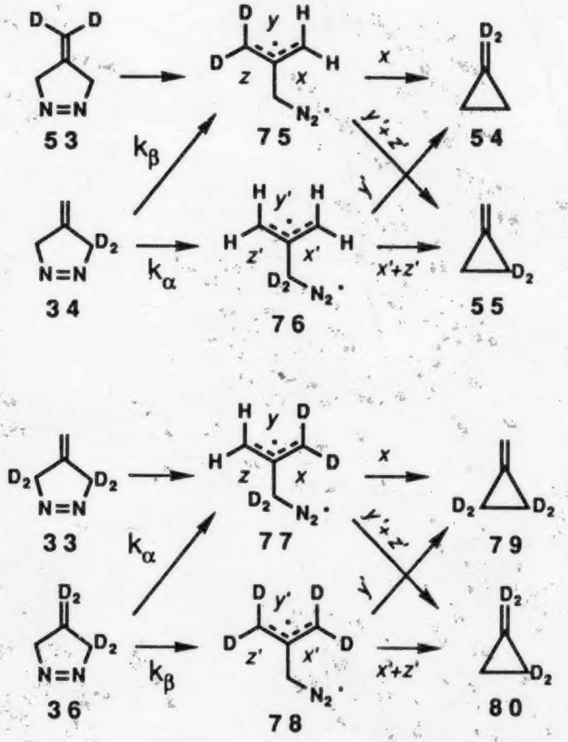
Accurate predictions for product ratios from the previous deuterated 4-methylene-1-pyrazolines can be made by using 3 modes of methylenecyclopropane ring closure from irreversibly formed diazenyl radical intermediate (Scheme 5). Modes *x* (closure between C_3 and C_5 of reactant) and *z* (closure between the diazenyl methylene and the exomethylene) are intramolecular S_H2 reactions. The *y* mode is considered[18] to be an electrocyclic ring closure between the two allylic termini, most likely with synchronous loss of molecular nitrogen. From Scheme 5 Chang and Crawford[17] determined the base *x*,y and *z* closure values for 4-methylene-1-pyrazoline **1** to have the ratio $k_x:k_y:k_z = 0.28:0.44:0.28$. Chemically, an equivalency of k_x and k_z means diazenyl radical intermediates **73** and **74** are of sufficient lifetime to allow rotamer equilibration of **73** and **74** (Eq. 20), i.e., backside S_H2 attack is equally probable for *x* and *z* closure. From the basis *x*:*y*:*z* ratios and by estimating the competition of CH_2 and CD_2 rotation out of an allylic plane at R=1.33 Crawford and Chang were able to predict product proportions for the thermolysis of **53**, **34**, **33**, and **36** to within 1% of the experimental values (Scheme 6).



Scheme 5



(Eq. 20)



Product Proportions	
Observed	(Calculated)
53	34
34 (35)	40 (40)
66 (65)	60 (60)
33	36
24 (25)	29 (30)
76 (75)	71 (70)

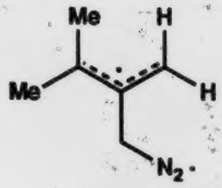
Scheme 6

Realizing that 3,3-dimethyl-4-methylene-1-pyrazoline **28** and 4-isopropylidene-1-pyrazoline **26** have three primary allylic carbons between them LeFevre and Crawford[5] re-examined their previous analysis

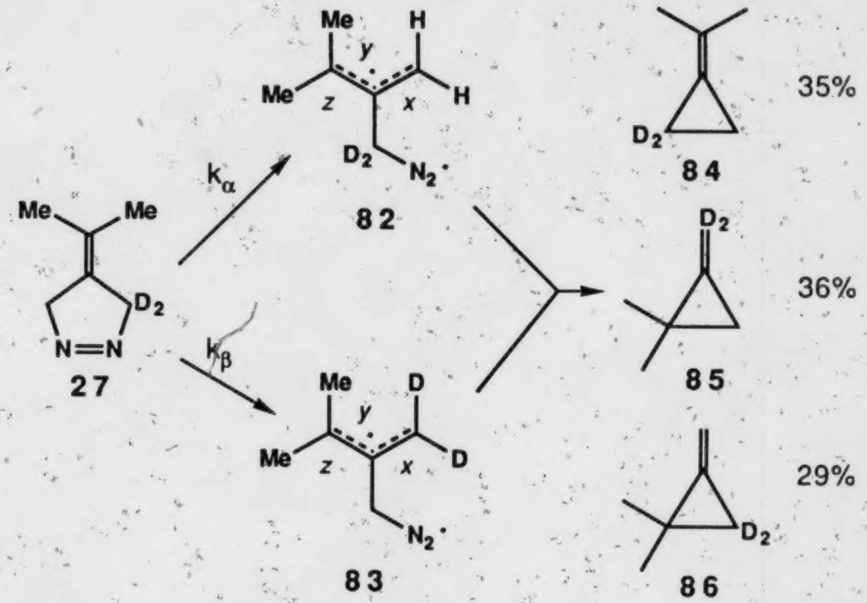
(Scheme 3) with the intent of determining whether Chesick diradical **66** actually exhibited the three modes of ring closure expected from diazenyl radical **81** (precursor to **66**). In terms of $\delta\Delta G^{\ddagger}$ per deuterium values, diazenyl radical intermediates are possible. A KIE of 1.12 ± 0.02 observed for **27** (Scheme 7) represents a free energy change of 51.8 ± 8 cal/mole per deuterium for a two bond homolysis, which is considerably less than the expected 90-120 cal/mole per deuterium[23]. When calculated as a single bond homolysis (Scheme 7) a KIE (k_α/k_β) of 1.27 ± 0.04 is obtained which represents a reasonable value $\delta\Delta G^{\ddagger}$ per deuterium (107 ± 14 cal/mole - see Eq. 7). From an analysis of Scheme 7 LeFevre and Crawford[5] were able to establish *x:y:z* values of 38:25:37 for 4-isopropylidene-1-pyrazoline **26**. They were then able to apply this ratio to the thermolysis of **29** (Scheme 8). Cleavage of the tertiary allylic C-N bond would form the diazenyl radical **82** while *beta* cleavage would initially form diazenyl radical **90** but would probably lose nitrogen quickly due to the stability of the 3° carbon to form the Chesick diradical **89**. In terms of these two intermediates and the previous *x:y:z* values the authors were able to predict a product ratio of 15:44:41 for **84:85:86** from **29**. Within experimental error these results are consistent with the experimental ratio of 16:44:40.

LeFevre and Crawford[5] were unable to predict accurate product ratios from the thermolysis of **27** (two primary allylic carbons) from the Chesick diradicals **87** and **88** which would be generated from **82** and **83** respectively.

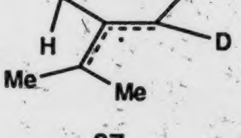
In summary, products from 4-alkylidene-1-pyrazolines with primary carbons in the 3 and 5 positions can be rationalized from a diazenyl radical that closes to form alkylidenecyclopropanes by S_H2 x and z modes and an electocyclic y mode. Crawford and Chang[18,17] have used this behavior as



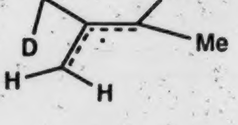
81



Scheme 7



87



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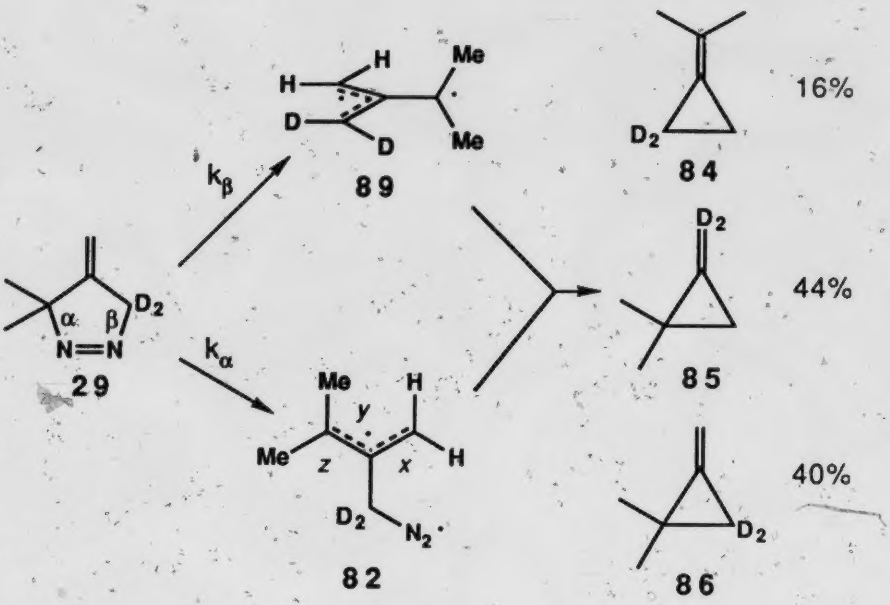
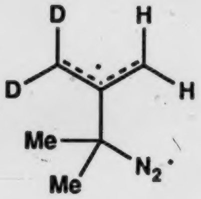


Scheme 8



90

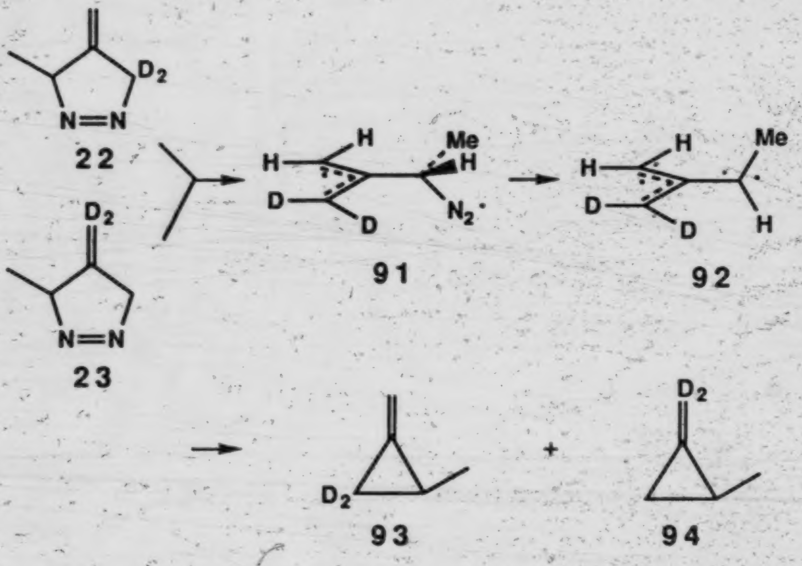
supportive evidence that compounds such as the deuterated 4-methylene-1-pyrazolines **33-36**, whose KIE give ambiguous conclusions with regard to one vs two-bond homolysis (Table 4), actually follow a one-bond cleavage process in the initial rate determining step.

Single-bond homolysis of dialkylated 4-alkylidenecyclopropanes form tertiary diazenyl radicals that quickly lose molecular nitrogen and develop products from Chesick diradical intermediates that react in accord with least motion principals. A mixture of the two product forming mechanisms appears to occur with compounds such as **29** that can form tertiary and primary diazenyl radicals.

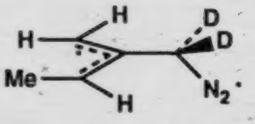
4-Alkylidene-1-pyrazolines With Obscure Mechanisms - Possible Theoretical Explanations

Difficulties arise when trying to rationalize the thermolysis mechanism of 4-alkylidene-1-pyrazolines with secondary C-N bonds. Since one bond homolysis would generate a secondary diazenyl radical with a stability in between that of tertiary and primary diazenyl radicals it is possible a mixture of mechanisms may be occurring. KIE for the thermolysis of deuterated 3-methyl-4-methylene-1-pyrazolines **22** and **25** (1.18 and 1.02 respectively) suggest that the C_5-N one-bond homolysis (Scheme 9) predominates[5]. Cleavage of the C_5-N bond of both **22** and **23** leads to the diazenyl radical intermediate **91** which might be expected to lose nitrogen quickly[23] to form the Chesick diradical **92**. Intermediate **92**, however, can not account for the 18-20 % of 4-ethylidenecyclopropanes that are produced. Product formation from the diazenyl radical **91** creates all the obtained products; however, proportions from **22** and **23** should be identical. Cleavage of the C_3-N bond of **22** and **23** produces non-identical pairs of primary diazenyl radicals (**95,96** and **97,98** respectively) which can account for product differences; however, the KIE of 1.02 for the analogous **32** is so small that significant contributions from C_3-N homolysis is improbable.

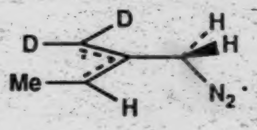
The product distributions from the thermolysis of other C_3 or C_5 methyl substituted 4-alkylidene-1-pyrazolines provide only a minor mechanistic insight. Compounds **99** and **108**[37] produce four alkylidenecyclopropane products **131-134** (Scheme 10). The results are



Scheme 9



95



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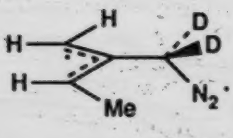

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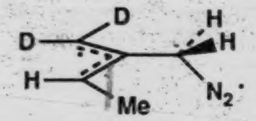
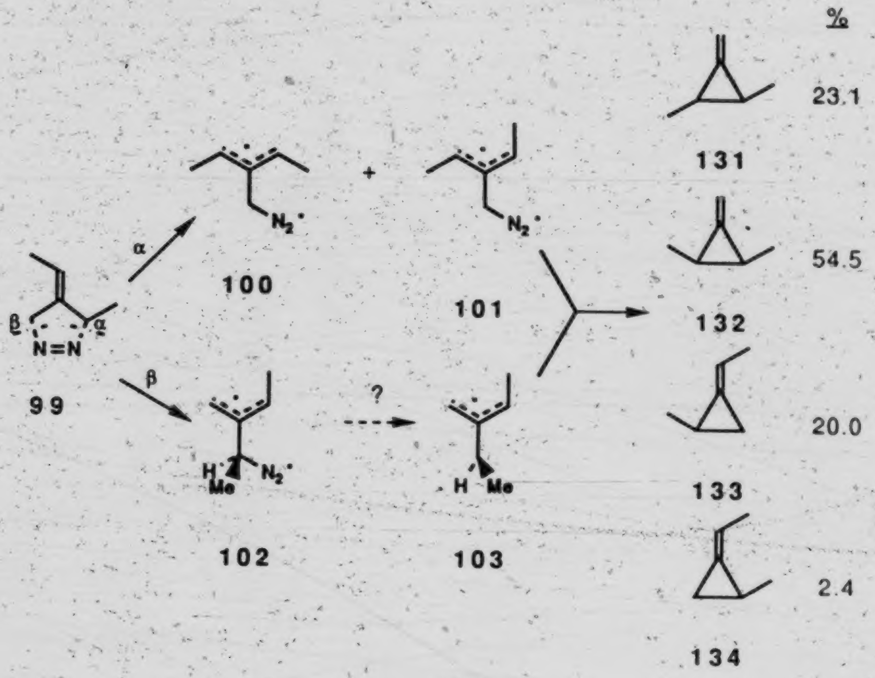


98

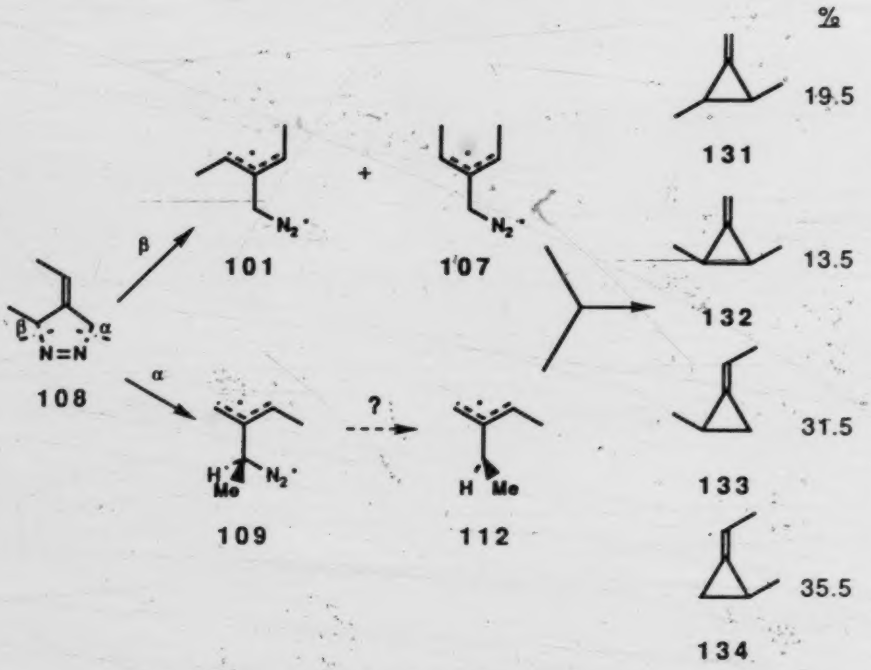
difficult to interpret, however, since three diazenyl radical intermediates are possible from each pyrazoline. Chang[24] has suggested that steric hindrance caused by the exocyclic methyl of **99** would lead to mainly α-cleavage and intermediate **100**. Furthermore, steric hindrance by methyls on C$_5$ and C$_6$ could suppress *x* and *z* closure, leading to more *y* closure and therefore the large yield 77.6% of 2,3-dimethylmethylenecyclopropanes **131** and **132**.



Scheme 10

Using steric hindrance rationalizations Chang[24] also predicted **111** to be the major intermediate from thermolysis of **108**. Closures from the *x* and *y* mode would lead to the 67% of ethylidenecyclopropanes **133** and **134**.

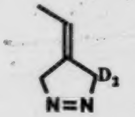
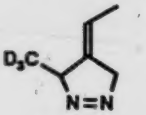
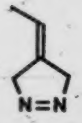
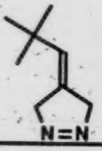
Regardless of these interpretations, the mechanistic understanding of C_3 and C_5 mono-methyl 4-alkylidene-1-pyrazoline thermolysis remains obscure. Analogies have been made[5,8] between the 4-alkylidenepyrazolines, and the 4-fluoromethylene- and 4-difluoromethylene-1-pyrazoline systems of Dolbier and Burkholder[8]. LeFevre and Crawford[5]



Scheme 11

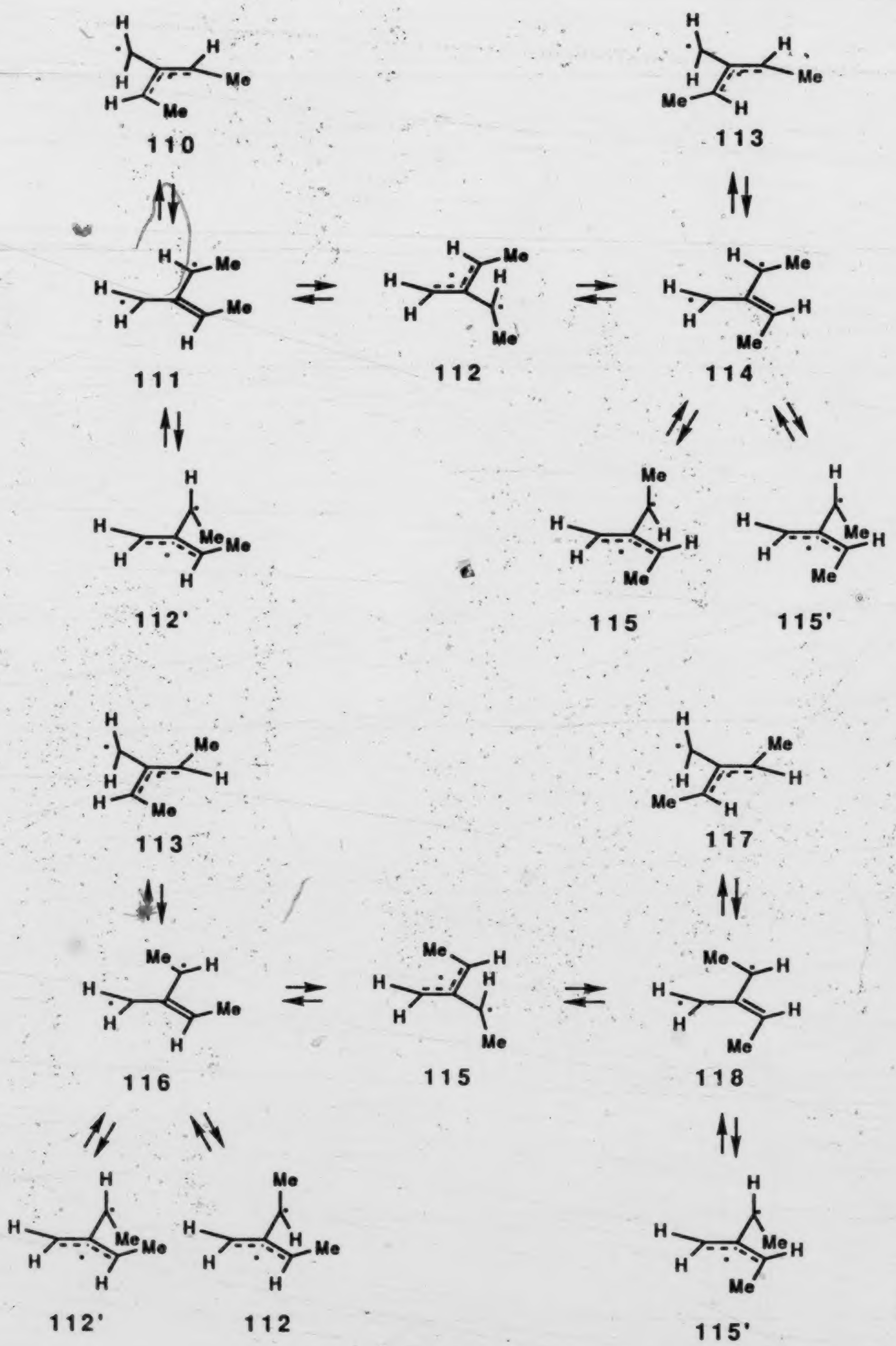
have observed that 4-alkylidene-1-pyrazolines with one alkyl substituent on the exocyclic methylene have a significant tendency for the exocyclic carbon to become a ring carbon (Table 7), as is the case for the exocyclic fluoromethylenes. Dolbier and Burkholder proposed that the thermolysis of 4-alkylidene-1-pyrazolines produces a set of partially equilibrating trimethylenemethane (TMM) species. "Subtle deviations from the symmetry of the parent (C_4H_6) TMM could give rise, either via E_a or $\Delta S^\ddagger$ differences, to the observed preferred cyclizations." In terms of the 3-methyl-4-ethylidene-1-pyrazolines a possible system of interconversions might be expected to occur as in Scheme 12. Which of the intermediates is first formed is dependent on the identity of the original pyrazoline and on the

Table 7 Percentage yield of products incorporating the exocyclic carbon of the reactant into the cyclopropane ring of the product.

Compound		% Cyclopropane	Ref
18		90	18
105		>92	37
17		>88	37
106		96	37

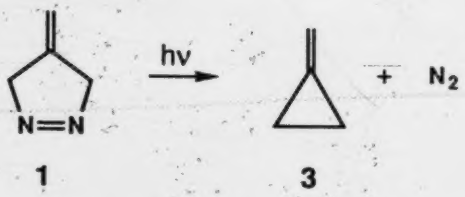
dynamics[38] of the loss of molecular nitrogen. The partial equilibrium allows for the observed "memory" of the original TMM produced.

Theoretical support for interconversion of orthogonal TMM **122** and planar C_{2v} TMM **123** is provided by Feller *et al.*[38] Their results are consistent with a ground state TMM that is triplet in nature (**120**) and lies 14-21 kcal/mole below the nearest singlet state[39]. Experimentally, one expects singlet states to be formed from the thermolysis of 4-alkylidene-1-pyrazolines. In confirmation it has been shown by Gajewski[40] that only methylenecyclopropanes are formed from the direct photolysis of 4-methylene-1-pyrazolines **1** which they propose produces a singlet TMM (Eq. 32). Triplet products **119** are formed only when **1** was

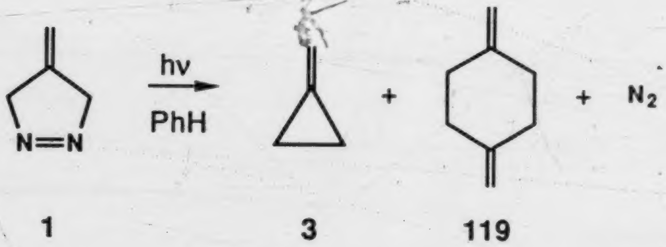


Scheme 12

photosensitized by benzene (Eq. 33). Gajewski proposed that photosensitized photolysis produces singlet and triplet TMM with a possible intersystem crossing from singlet **121** to triplet **120**. Feller *et al.*[38], however were unable in their MCSCF calculations to find an intersystem crossing point below the singlet TMM **122**. Dimer products **119** are not produced from the thermolysis of 4-alkylidene-1-pyrazolines thus the formation of triplet intermediates is unlikely.

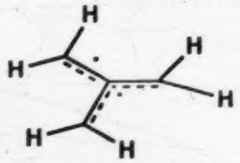


(Eq. 32)

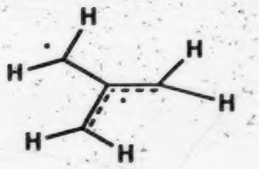


(Eq. 33)

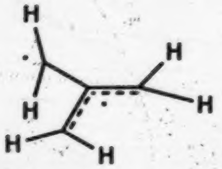
The lowest singlet TMM found by Feller *et al.*[38] and others[41,42] is the orthogonal TMM **122**. Feller has calculated, however, that the planar singlet TMM **123** is close enough in energy to allow interconversion between the orthogonal and planar singlet TMM, and methylenecyclopropane (MCP) formation is possible from each.



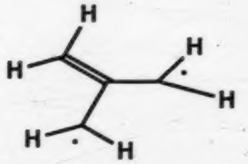
120
planar triplet
D_{3h}



121
planar singlet
C_{2v}

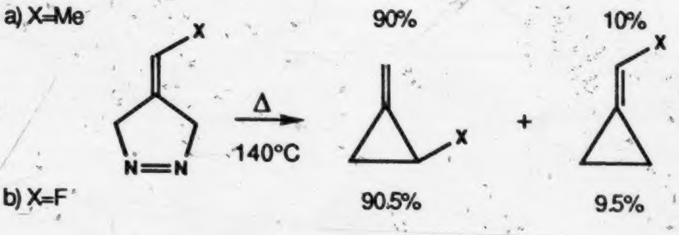


122
orthogonal singlet
C_{2v} ($^1B_1$)



123
planar singlet
C_{2v} ($^1A_1$)

More recently Dolbier[7] has extended the suggestion by Carpenter[43] that molecular reaction dynamics can significantly influence product formation. Carpenter suggested that a conservation of momentum, particularly with regard to small molecules, can carry a homolysis reaction past the intermediate stage directly to the product in the closest straight line path. Noting the similarity in product ratios for the thermolysis of 4-ethylidene-1-pyrazoline **124a** and 4-fluoromethylene-1-pyrazolines **124b** (Eq. 34), Dolbier proposed that the similar masses of F- and H_3C- could lead to similar products by a conversion of momentum. In the absence of strong influences such as electronic effects, Dolbier states that "nonconcerted homolytic processes involving formation or destruction of a diradical species and when overt steric effects do not play a role in such systems, more subtle influences can and will be observable".

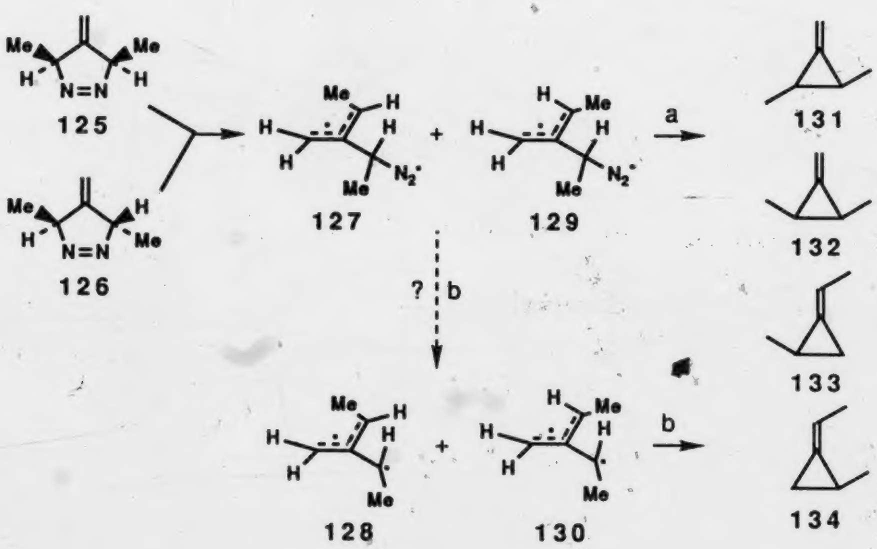


124

(Eq. 34)

A diasteriomeric product study of *cis*- and *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **125** and **126** respectively may provide clues as to the product forming mechanism of mono-alkylated 4-alkylidene-1-pyrazolines. In particular, the study may suggest why **99** produces 54.5 % of **132** and only 2.4 % of **134**, while **108** produces 13.5 % and 35.5 % respectively. The thermolysis of the 3,5-dimethyl-4-methylene-1-pyrazolines have the advantage that each C-N bond is kinetically equivalent, thus, the question of one-bond homolysis partitioning does not exist. Also, thermolysis of **125** and **126** should each produce an identical pair (though not necessarily the same ratio) of diazenyl radical intermediates **127** and **129** making product rationalization easier.

In order to ascertain the possibility of a partly equilibrating system of intermediates as in Scheme 12, or to ascertain whether products originate from Chesick diradicals, it is necessary to establish the loss of nitrogen from a proposed diazenyl radical intermediate. The presence of diazenyl radicals has been observed in the previously mentioned "turnaround" products (Eq. 10) of Engel and Gerth[20]. Dannenburg and Rocklin[22] have calculated a distinct barrier 14.0 kcal/mole to the decomposition of the ethyldiazenyl radical; however its lifetime would be short. A 12 ± 2 ns estimate of the lifetime of the primary methyldiazenyl radical has recently been made by Adams *et al.*[1] using Raman spectroscopy. Since the lifetime of a diazenyl radical is likely dependent on the stability of the resulting alkyl radical[20], thermolysis of C_3 or C_5 mono-alkylated 4-alkylidene-1-pyrazolines should have a lifetime inbetween that of the primary diazenyl radical from which MCP are proposed to form directly[17,18], and that of the tertiary diazenyl radical that loses nitrogen before MCP formation occurs[29]. A complete steriochemical analysis of MCP obtained from a chiral *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126** might determine the presence of a possible diazenyl radical during product formation (path "a" in Scheme 13) since inversion of stereochemistry is expected during an S_H2 reaction.



Scheme 13

OBJECTIVE

In this work optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline and *cis*-3,5-dimethyl-4-methylene-1-pyrazoline were synthesized. A complete stereochemical analysis of the alkylidenecyclopropanes obtained from the thermolysis of the optically active *trans* pyrazoline and a diastereomeric analysis of the alkylidenecyclopropanes obtained from the thermolysis of the *cis* pyrazoline were performed.

A complete stereochemical analysis of the alkylidenecyclopropanes obtained from the thermolysis of optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline should indicate product formation from a diazenyl radical in a one-bond cleavage mechanism since inversion of stereochemistry at the S_H2 center would occur.

It is theoretically possible to generate optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline by resolving the enantiomers of a synthetic precursor on a chiral HPLC column followed by synthetic steps that retain optical activity. Resolution of protected 4-methylene-1-pyrazolidine synthetic precursors was achieved.

The absolute stereochemistry of the optically active pyrazoline was determined by the extrapolation of the absolute configurations observed in similar pyrazoline structures and by the x-ray structure of a solid synthetic precursor. The absolute stereochemical configurations of the product *trans*-2,3-dimethylmethylenecyclopropane and E-2-methylethylidenecyclopropane have been previously determined. Extrapolation to the absolute configuration of Z-2-methylethylidenecyclopropane should be possible.

A diastereomeric analysis of the products obtained from the thermolysis of synthesized *cis* and *trans*-3,5-dimethyl-4-methylene-1-

pyrazoline will add to the library of alkylidenecyclopropane product ratios obtained from other dimethyl substituted 4-methylene-1-pyrazolines. Mechanistic rationalization of the products obtained from the target pyrazolines should be simplified in comparison to previous studies since both C-N bonds are kinetically equivalent and should produce only two intermediates in a one-bond cleavage mechanism. Mathematical solutions were not found however.

Synthetic precursors of the diastereomeric 3,5-dimethyl-4-methylene-1-pyrazolines was generated concurrently as a mixture. Separation of diastereomeric precursors followed by non-epimerizing synthetic steps lead to nearly diastereomerically pure 3,5-dimethyl-4-methylene-1-pyrazolines.

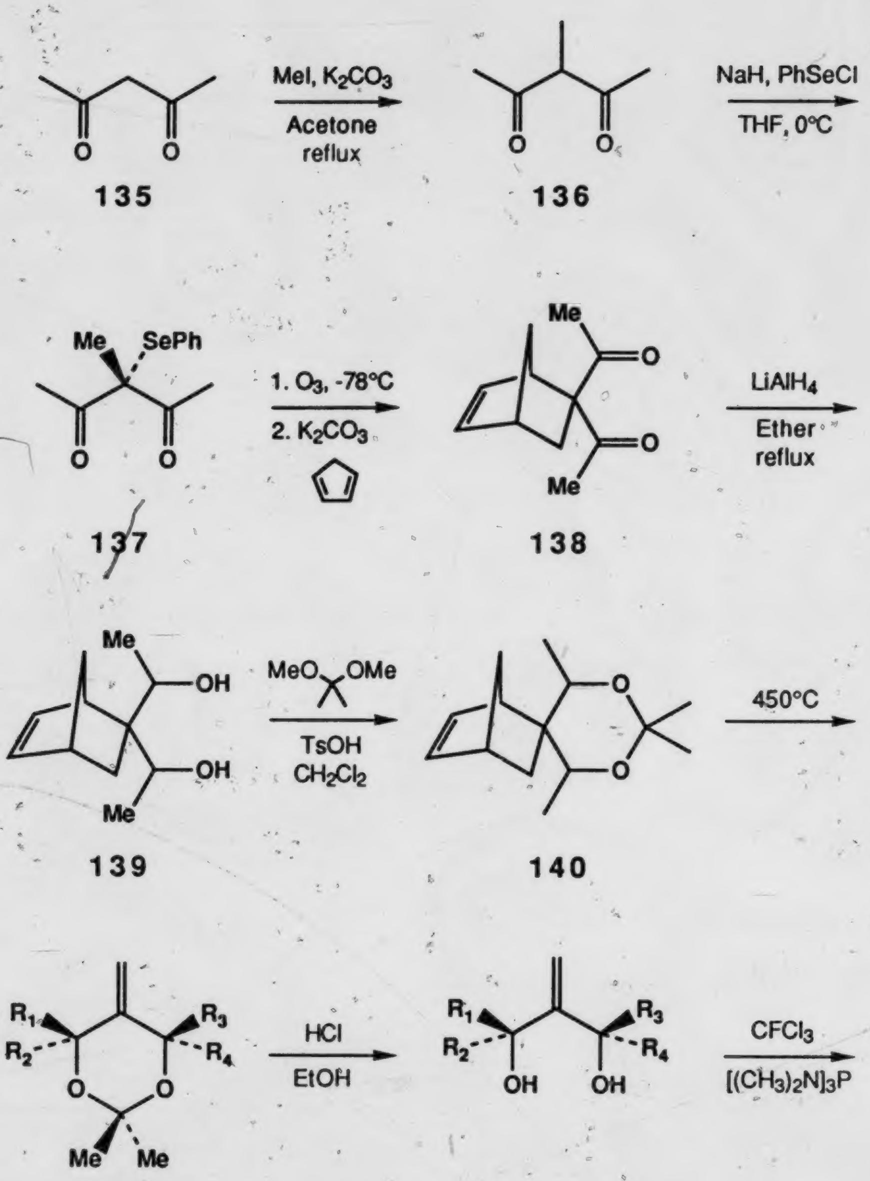
An estimate of the 3,5-dimethyl-4-methylene-1-pyrazoline thermolysis rate constants was obtained to signal a possible deviation from the expected one-bond homolysis mechanism.

SYNTHESIS

3-Methyl-2,4-pentanedione **136** (Scheme 14) was prepared[44] by refluxing a mixture of acetylacetone **135**, methyl iodide, and potassium carbonate in acetone for 3 h. The precipitation of the resulting potassium iodide was aided by dilution of the solution with a 1:1 mixture of acetone/ether as was suggested by Roe and Harbride[44]. A GC analysis indicated the presence of 6% of a higher molecular weight compound which was assumed to be 3,3-dimethyl-2,4-pentanedione. This impurity was removed by careful distillation on a spinning band column giving pure **136** as indicated by ^{1}H NMR.

Using the fairly general procedure of Renga and Reich[45], 3-methyl-3-phenylseleno-2,4-pentanedione **137** was then generated in high yield (81.5%). Sodium hydride selectively removed the more acidic C_3 proton of 3-methyl-2,4-pentanedione **136**. Nucleophilic displacement of chloride ion from benzeneselenenyl chloride by the resulting β-ketoenolate was readily accomplished at 0°C. The reaction was quickly quenched by pouring the mixture into an aqueous sodium bicarbonate solution. Although the reaction time was not optimized, a reaction time of >30 minutes led to a decrease in yield probably as a result of the extreme sensitivity of the product selenide to nucleophilic attack[46]. The product 3-methyl-3-phenylseleno-2,4-pentanedione **137**, purified by recrystallization, was readily identified by its ^{1}H NMR singlets at 2.33 and 1.54 ppm and its aromatic multiplet.

The oxidation of selenide **137** was accomplished at -78°C by bubbling freshly generated ozone through a dichloromethane solution of **137**. Since over-oxidation of a selenide to the selenoxide does not readily occur at -78°C[47], the stoichiometric addition of ozone was detected by the



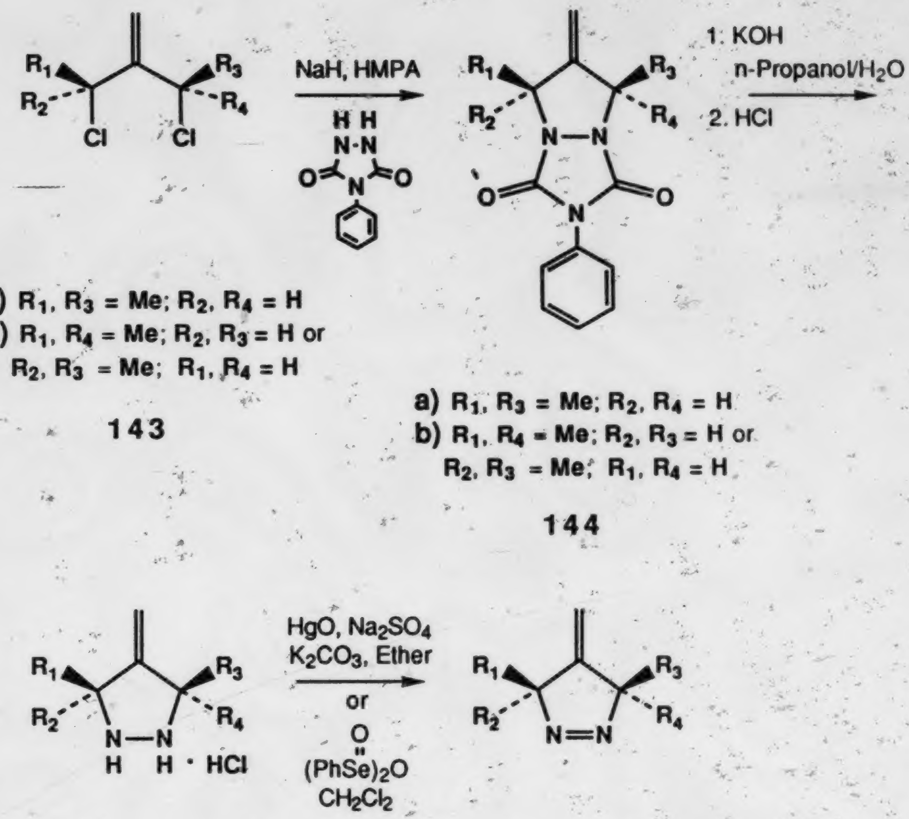
135 136 137 138 139 140

a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = H

141

a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = H

142



a) $R_1, R_3 = Me; R_2, R_4 = H$
b) $R_1, R_4 = Me; R_2, R_3 = H$ or
$R_2, R_3 = Me; R_1, R_4 = H$

143

a) $R_1, R_3 = Me; R_2, R_4 = H$
b) $R_1, R_4 = Me; R_2, R_3 = H$ or
$R_2, R_3 = Me; R_1, R_4 = H$

144

a) $R_1, R_3 = Me; R_2, R_4 = H$
b) $R_1, R_4 = Me; R_2, R_3 = H$ or
$R_2, R_3 = Me; R_1, R_4 = H$

145

125 $R_1, R_3 = Me; R_2, R_4 = H$
126 $R_1, R_4 = Me; R_2, R_3 = H$ or
$R_2, R_3 = Me; R_1, R_4 = H$

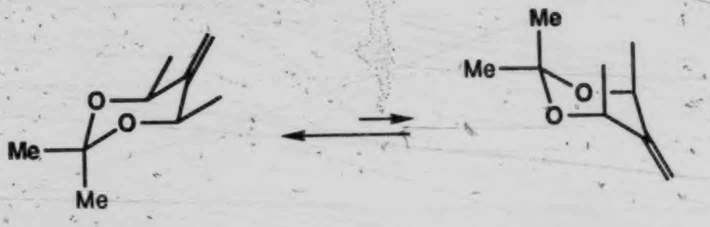
Scheme 14

formation of a blue solvent tint (excess O_3). Warming the solution resulted in the *syn* elimination of the highly reactive selenoxide to generate 3-methylene-2,4-pentanedione. Since 3-methylene-2,4-pentanedione was too unstable to isolate it was trapped with cyclopentadiene as a Diels-Alder adduct while in the presence of potassium carbonate. A non-nucleophilic base was required in order to remove any benzeneseleninic acid produced as a by-product of the *syn* elimination. Product 5,5-diacetyl-2-norbornene **138** was readily purified in 76.4% yield by the distillation of the heterogeneous mixture. The product was identified by its molecular weight as determined by mass spectrometry (178.0980) and its ^1H NMR spectra. Infrared spectrometry indicated a symmetrical and unsymmetrical carbonyl stretch at 1695 and 1710 cm^{-1}.

The oxidation-reduction sequence was also possible from the impure **137** obtained after solvent evaporation (yellow oil) with a 5-15% reduction in yield.

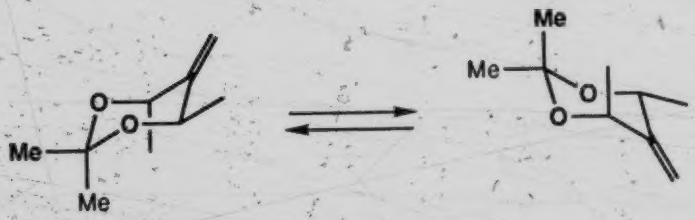
In an effort to maximize the yield of 5,5-bis-(1-hydroxyethyl)-2-nonbornene **139** that would eventually produce *rac*-2,2,4,6-tetramethyl-5-methylene-1,3-dioxane **141b** (2 of 4 diastereomers of **139**), 5,5-diacetyl-2-norbornene **138** was reduced using a variety of reducing agents. Since isomer identification of **139a** and **139b** would have been difficult, the final diastereomeric *rac/meso* ratio of **141** was measured (6.2 m OV101 GC column). The two possible diastereomers of **141** (**141a** and **141b**) were readily identified by ^1H NMR. As can be seen in Eq. 35, chair inversion of **141a** produces two conformers on which the C_4 and C_6 methyls are either both equatorial **141a'** or both axial **141a"**. Because of the stability of the diequatorial conformer only **141a'** is experimentally observed. Its two diastereomeric C_2 methyls are seen as two ^1H NMR singlets (1.57 and

1.41 ppm). Chair inversion of the *rac* isomer (Eq. 36) interchanges the axial and equatorial positions of the C_4 and C_6 methyls and also of the two diastereotopic C_2 methyls. Since the two conformers **141b'** and **141b"** are energetically identical, rapid chair inversion ~~occurs leading~~ to a coalescence of the two C_2 methyl singlets, i.e., only one singlet at 1.39 ppm is seen in an ^1H NMR spectrum (293K).



141a' **141a"**

(Eq. 35)



141b' **141b"**

(Eq. 36)

The stereoselectivity exhibited by the reducing agents was virtually identical (43-52% *rac* as the acetal **141b**), thus reaction yield determined the best procedure (Table 8). The best reduction in terms of both yield (94% as the diol **139**, 81% overall with diol **139** protected as the acetal **141**) and stereoselectivity (52% *rac* acetal **141**) was achieved with lithium aluminum hydride in refluxing ether by using an adaption of the

Table 8 Stereoselectivity of dione **138** reduction.

Reducing Agent	Conditions	% *rac*-**141b**	Yield **141**
$LiAlH_4$	1.4 eq./34°C	52	81
Red Al	1 eq./0°C	44	42.9
"	2 eq./0°C	43	54.6
"	1 eq./-78°C	46	75.9
Dibal	2.8 eq./-78°C	46	71.6

procedure of Maier, Roth, and Schmidt[48]. Lengthy reflux times did not appear to decrease the yields. After a standard workup I.R. spectra indicated a total loss of any carbonyl stretch and a gain of a broad O-H stretch at 3290 cm^{-1}. Although it was impossible to definitely establish the number of diastereomers produced by ^1H NMR, ^{13}C NMR accounted for 43 of the possible 44 lines if 4 diastereomers of **139** were present. An elemental analysis indicated that the diol elemental composition matched closely to that of the theoretical composition.

Dibal (-78°C) provided a good yield at 71.6% as the acetal **141** (Table 8). Since the Lewis acid Dibal can provide only one hydride ion per molecule, at least two equivalent of Dibal was needed (2.8 equivalent used).

While Dibal might favor attachment and delivery of its hydride ion to the same carbonyl group, Red Al (sodium bis-(methoxyethoxy)-aluminum hydride) can provide two hydride ions. Therefore the possibility existed for the second hydride to be delivered to the β-carbonyl intramolecularly and thus produce some stereoselectivity. Reaction conditions that might promote this type of selectivity, i.e., 1 equivalent of Red Al added to diketone **138** at -78°C and 0°C, did not produce any additional stereoselectivity. Using 2 equivalent of Red Al at 0°C produced similar results. The reduction at -78°C produced a yield of 75.9% at the acetal **141** stage, while raising the temperature to 0°C gave yields of 34.6% and 42.9% as the acetals **141** from 1 and 2 equivalents of Red Al respectively.

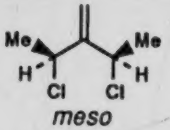
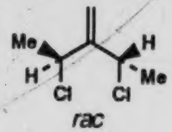
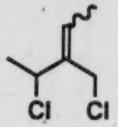
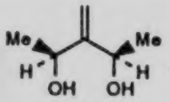
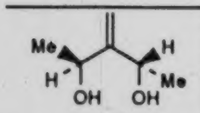
The acid catalyzed protection of diol **139** was readily accomplished in consistently high yields (88-95%) at room temperature by using a large excess of 2,2-dimethoxypropane. Distillation of the product produced pure 5,5'-spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene **140** as four diastereomers. I.R. spectra indicated a total loss of the alcohol O-H stretch and the presence of a gem-dimethyl symmetric and asymmetric C-H stretch. ^{13}C NMR produced all 56 lines that were expected as the result of the production of 4 diastereomers.

Acetal **140** was pyrolyzed at approximately 450°C using an adaption of the procedure of Corey and Suggs[49]. Unreacted **140** that could not be vapor transferred out of the primary cold trap at 0°C was re-thermolyzed in order to increase the overall yield. A spinning band distillation was required to separate **141** totally from the by-product cyclopentadiene. The product 2,2,4,6-tetramethyl-1,3-dioxane **141** had to be handled carefully due to its volatility. Periods of storage greater than one month at -20°C led to deterioration of **141**. Acetal **141** was separated into its *meso* and *rac* forms by a 230-400 mesh flash silica column impregnated with 17% silver nitrate. It was necessary to rerun a small portion of the eluent since some overlap of the two isomers occurred. Careful distillation using a long 30 cm vigreux column removed the majority of solvent ethyl acetate and hexane.

Using a modification of the procedure of Salomaa and Kankaanpera[50] the deprotection of acetal **141** to generate diol **142** was carried out with 0.3N hydrochloric acid as a catalyst in 95% ethanol (5 ml of 3N HCl in 50 ml of 95% ethanol). This procedure, when carried out at room temperature, did not give any indication of tautomerization of the olefin function and allylic S_N2 displacement of an oxonium ion, i.e., isomeric purity was retained. I.R. spectra revealed a large O-H stretch at 3340 cm^{-1}. Although high resolution mass spectrometry did not produce a parent peak, it did reveal the presence of a fragment with m/e at 101.0590 which could occur as a result of the loss of an allylic methyl group. Chemical ionization did produce a parent + NH_4^+ peak. ^{1}H NMR indicated that only one diol **142** isomer was obtained, i.e., the original stereochemistry was most likely retained.

The mild carbon tetrachloride/triphenylphosphine reagent system and its variants were used to convert diols **142** into their respective dichlorides **143** in an attempt to minimize epimerization of the two allylic stereocenters of **142** and to minimize the formation of the S_N2' product **147** (Table 9). Optimum conditions were not found. From the data in Table 9 it is difficult to establish distinct patterns resulting from a change in the reaction conditions using the reagents carbon tetrachloride and triphenylphosphine. While regioselectivity seems to be the poorest for chlorination of the *meso* diol **142a** (21% of **147** produced when the reaction temperature was 65°C), this did not appear to be the case for the *rac* diol **142b**. A similar chlorination of the *rac* diol at 40°C resulted in no epimerization and 11% of **147**. Surprisingly, a decrease in temperature to 25°C produced 6% of the epimer **143a**. The latter reaction time, however, was increased by 350%.

Table 9 Stereoselectivity and regioselectivity observed in the clorination of diol142

Diol	Chlorinating Agent	Conditions	% Yield			% Total Yield
			 *meso* **143a**	 *rac* **143b**	 **147**	
 *meso* **142a**	Ph_3P/CCl_4	65-70°C 100 min.	69	10	21	70
	$[(CH_3)_2N]_3P$ $CFCl_3$	0°C/15 min 23°C/2h	80	18	2	36
 *rac* **142b**	n-Bu_3P/CCl_4	0°C/0.5h 23°C/40h	14	61	25	42
	Ph_3P/CCl_4	40°C/7h	0	89	11	62
	Ph_3P/CCl_4	60°C/3.5h	12	79	9	52
	Ph_3P/CCl_4	25°C/24h	6	85	9	58

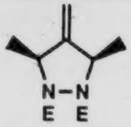
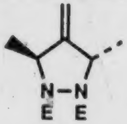
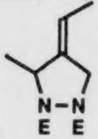
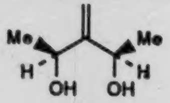
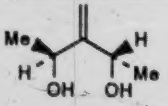
The combination of tributylphosphine and carbon tetrachloride gave a low yield (42%), the poorest regioselectivity (25% **147**) and 14 % epimerization product.

The literature[51] indicates that the combination hexamethylphosphorus triamide/carbon tetrachloride produces the largest amount of unrearranged product from α-alkylallyl alcohols. In a similar reaction but with trichlorofluoromethane replacing the the less volatile carbon tetrachloride the *meso* diol **142a** produced only 2% of **147**, however a relatively large amount of epimer **143b** (18%) and a reduced yield (36%) was obtained. After considering the possibility that the lengthy workup of the dichloride could be at least in part responsible for poor yields and poorer regio- and stereoselectivity, one-pot reactions generating the triazolinedione **144** from diol **142** was attempted (Table 10). In terms of the overall yield (48%) this method gave superior results for the *rac* diol and better than average results in terms of regioselectivity (22% **148**) and stereoselectivity (8% **144a**) than was obtained by a two step synthesis where the intermediate dichloride was isolated. The same reagents produced poorer yields for the *meso* diol **142a**.

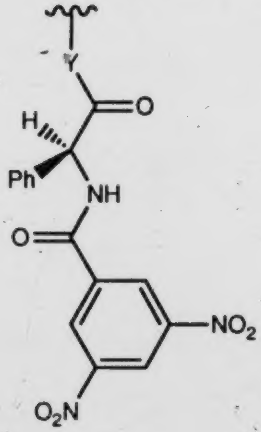
The generation of the triazolinedione **144** directly from dichloride **143** gave 50-55% yields (Table 10). A large amount of S_N2' product **148** (25-31%) exceeding that initially present in the dichloride (2-9%) was obtained.

The active component of the chiral DPG HPLC column (supplied by Regis Chemical Company) is shown in structure **149**. In order to obtain molecular chirality recognition geometric considerations require that a minimum of three simultaneous interactions occur between the chiral dinitrophenylglycine (DPG) and the system of interest[52]. Since

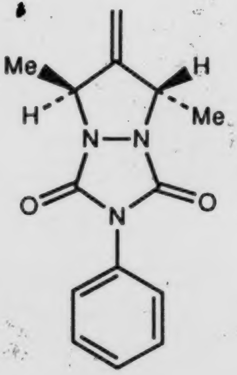
Table 10 Stereoselectivity and regioselectivity observed in the synthesis of triazoline diones **144**

Reagent Diol or Dichloride(s)	Chlorinating Agent Conditions	% Yield			% Total Yield
		 *meso* **144a**	 *rac* **144b**	 **148**	
meso **143a** - 80% *rac* **143b** - 18% **147** - 2%		63	12	25	55
 *meso* **142a**	$CFCl_3/[(CH_3)_2N]_3P$ 23°C/3h	54	14	32	18
rac **143b** - 85% *meso* **143a** - 6% **147** - 9%		8	62	31	50
 *rac* **142b**	$CFCl_3/[(CH_3)_2N]_3P$ 23°C/2h	8	70	22	48

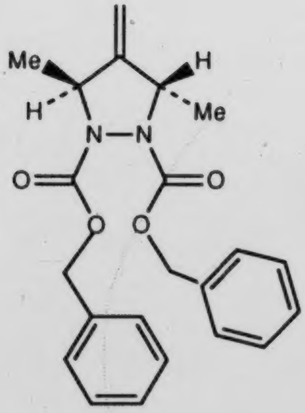
enantiomeric and diastereomeric selectivity was needed in order to purify a possible mixture of stereo and geometric isomers, i.e., **144a, 144b,** and **148** (see Table 10), several pyrazolidine protecting groups were considered, each resulting in compounds with features that might interact with the chiral DPG HPLC column. Each protected pyrazolidine considered (**144, 150, 151**, and **152**) contained an aromatic ring for π interactions, carbonyl and amino functions for polar and hydrogen bonding interactions, and also chiral centers for the most crucial chiral interactions.



149



144



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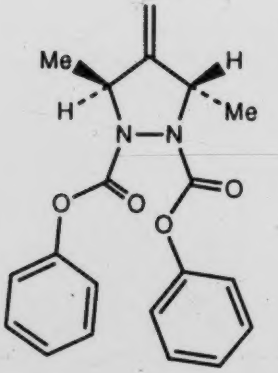
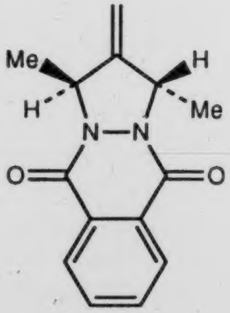
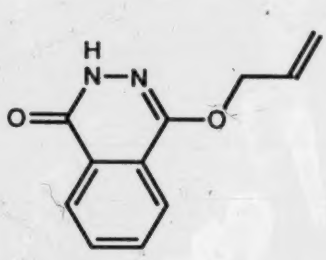


151

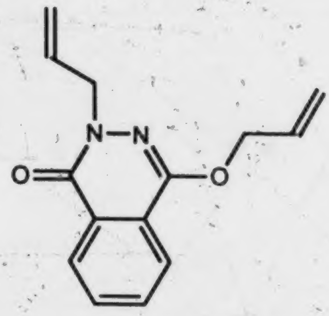


152

Although the flat structure of **152** might have topological benefits, an attempt was not made to generate compound **152** since model studies showed that the reaction of allyl bromide and phenylhydrazide generated primarily **153** and **154**, i.e., O-alkylation was a major problem.



153



154

Using a modification of the procedure of Rubottom and Chabala[53], the reaction of phenylhydrazodicarboxylate with dichloride **143** did not produce any compound **150**, however phenol and unreacted **143** were isolated. Since the phenol generated was likely caused by the stability of the phenoxide ion, a carbamate with a benzoyl group was tried. Using a modification of the above procedure the reaction of benzylhydrazodicarboxylate with *rac* dichloride **143b** gave ~10% of the *rac*-pyrazolidine **150**. The major product was the S_N2' product E-1,2-dicarbenzoxy-3-methyl-4-ethylidenepyrazolidine (~19%). Some enantiomeric separational preferences for the racemic **150** was shown by the chiral DPG HPLC column.

The best candidate in terms of overall yield and regioselectivity was the cyclic 4-phenylurazole with an overall yield of ~39% of the racemic **144b** and an overall yield of 50-55% of protected pyrazolidine compounds

144 and **148**. The three diastereomers **144a, 144b** and **148** and the enantiomers of **144b** were separated by recycling the material through a chiral DPG HPLC column with a 35% isopropanol/hexane solution and saving leading and tailing edges. The compounds **144a** and **144b** were fully characterized. Positive assignments of the stereochemistry of diastereomers **144a** and **144b** was established by x-ray crystallography of (-)**144b** (Figure 1). The negatively rotating isomer was determined by x-ray crystallography to have the R,R,- configuration. (See Appendix C).

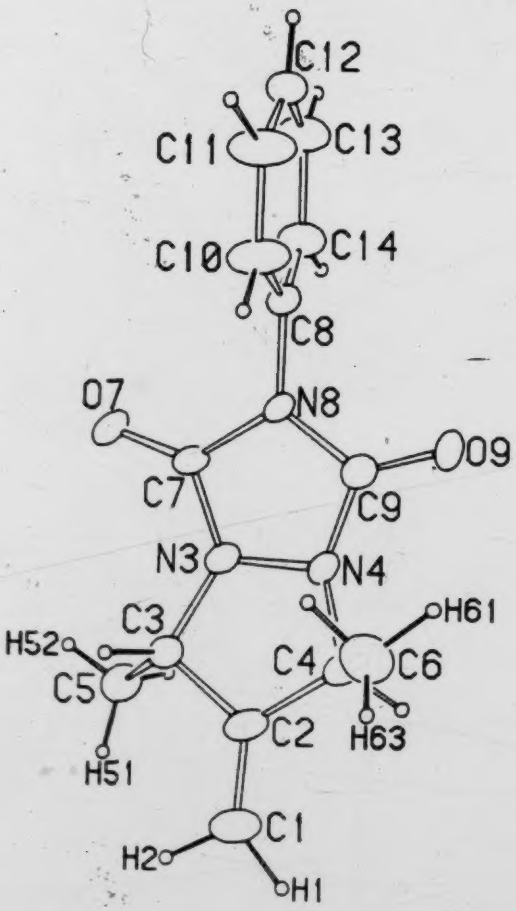
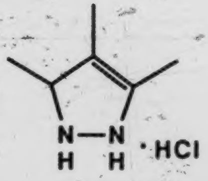


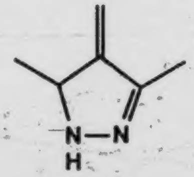
Figure 1 X-ray structure of **144b**

The hydrolysis of 98% isomerically pure triazolinedione **144** and acidification of the resulting pyrazolidine produced the pyrazolidine hydrochloride **145** with an isomeric purity of 98% (determined by ^{1}H NMR) and by-product aniline hydrochloride. The heterogeneous n-propanol/H_2O/KOH hydrolysis process was aided by a small amount of phase transfer catalyst tetrabutylammonium iodide. An argon atmosphere and the addition of EDTA were used to retard oxidation of the product pyrazolidine. ^{1}H NMR did not indicate the presence of the tautomer **155**.

Oxidation of the isomeric pyrazolidine hydrochlorides **145a** and **145b** in the presence of the aniline hydrochloride impurity was carried out using two methods. ^{1}H NMR analysis indicated that the tautomer **156** was not produced and that epimerization of the allylic centers did not occur by either method, i.e., oxidation of each isomer produced only one methyl doublet, one methyne multiplet, and one methylene triplet. The mercuric oxide oxidation (an adaption of the procedure of Crawford and Tokanaga[29]) was carried out at 5°C by stirring a mixture of sodium sulphate, anhydrous potassium carbonate, and the hydrochloride for 36 h. Aniline was then removed by acid extraction.



155

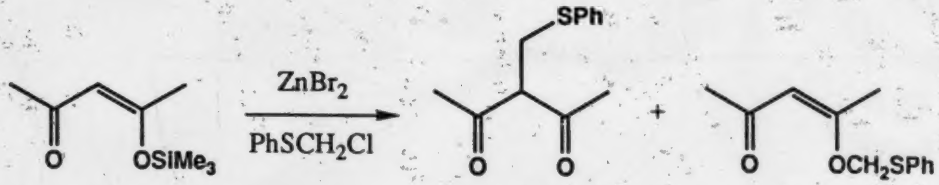


156

Oxidation of the *trans* isomer **145b** was also achieved by using an adaption of the procedure of Barton, Lester and Ley[54]. Unlike the lengthy mercuric oxide oxidation, the reaction was achieved in only 7 minutes with excess benzeneseleninic anhydride. It was necessary to add the strong base DABCO prior to the oxidation in order to remove any benzeneselenenic acid by product[47] which, when present, drastically reduced the yield possibly by addition to the pyrazolidine or pyrazoline olefin. Flash distillation of the product removed all of the aniline, however DABCO sublimed at the same time. Acid or neutral extraction removed this impurity. The final yield was 53%. Mass spectrometry indicated that the product had the expected molecular weight of 110.0841. The presence of optical activity in the *rac*-3,5-dimethyl-4-methylene-1-pyrazoline **126** generated from chiral **144b** confirmed the stereochemical orientation of its α-allylic centers. A detailed discussion of the thermolysis of *cis* and *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **125** and **126** is covered in the section on results.

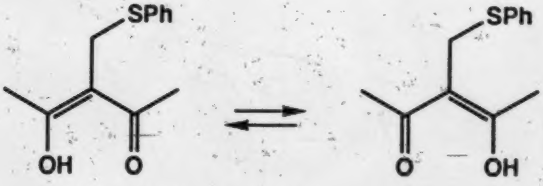
Attempted Methodologies

Encouraged by Paterson and Fleming's[55] successful *alpha* phenylthiomethylation of silyl enol ethers, an adaption of their methodology was used to phenylthiomethylate the silyl enol other of 2,4-pentanedione in the C_3 position (**157** in eq. 37). Reduction of the dione **158** and protection of the resulting diol as an acetal, followed by an oxidation/elimination sequence would then have produced 2,2,4,6-tetramethyl-5-methylene dioxane **141** (Scheme 14). The reaction of silyl dienol ether **157** with phenylthiomethyl chloride in the presence of a catalytic amount of zinc bromide produced approximately 10% of a mixture of the desired product **158** and an O-alkylated product **159**. Compound **158** was identified by the expected mass of 222.07075 and by its ^{1}H NMR spectra which indicated aromatic proton peaks and three singlets (see **160**). IR indicated a broad O-H stretch at >3200cm^{-1}. Compound **159** had no O-H stretch and had non-equivalent methyl groups as indicated by ^{1}H NMR. Since the reaction of 2,4-pentanedione with one equivalent of sodium hydride and then phenylthiomethyl chloride produced similar results, it is possible that the intermediate enolate ion of 2,4-pentanedione was too stable for further reaction with phenylthiomethyl chloride.



157 **158** **159**

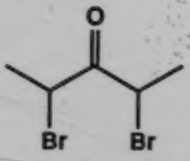
(Eq. 37)



160

2,4-Dibromo-3-pentanone **161** is structurally similar to the hydrochloride of 3,5-dimethyl-4-methylene-1-pyrazolidine **145** (Scheme 14) and is thus an attractive possible precursor of **145**. The reaction of the Wittig reagent methylenetriphenylphosphine with **161** (to form **162**) resulted in a large amount of white precipitate that was identified as methyltriphenylphosphonium bromide and unreacted **161** - probably occuring as a result of the acidic nature of the *alpha* proton. An attempted nucleophilic displacement of **161** with deprotonated 1,2-dicarbethoxy–

hydrazine (to generate **163**) also resulted in an acid-base reaction. The precipitate formed was identified as unreacted 1,2-dicarbethoxyhydrazine. Unreacted **161** was also isolated. The nucleophilic displacement of bromide in **161** with the less basic hydrazine monohydrate to form 3,5-dimethyl-4-pyrazolidone **164** was also unsuccessful. The resulting products were hydrazine hydrobromide and an unidentified organic product that was volatile enough to be lost on the rotoevaporator during workup.



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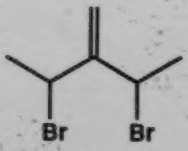

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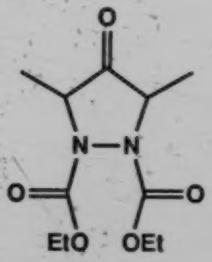
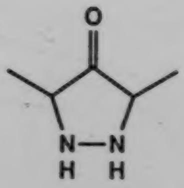
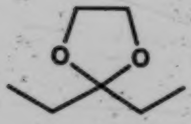


163



164

In an effort to reduce the acidity of the *alpha* protons of 2,4-dibromo-3-pentanone **161** was protected as the acetal **166**. The *p*-toluenesulfonic acid catalyzed reaction of ethylene glycol with 3-pentanone produced **165** in high yield. Further reaction of **165** with bromine using the procedure of Giusti and Morales[56] generated 2,2-bis(1'-bromoethyl)-1,3-dioxolane **166** in 91.5% yield. The presence of 9 lines in the ^{13}C NMR and duplicate peaks (different intensities) in the ^{1}H NMR indicated that two isomers were formed. As was expected, the nucleophilic displacement of the "neopentyl" bromide was difficult. Some reaction of **166** with 1,2-dicarbethoxyhydrazine anion in HMPA occured after 72 h at 60°C, however significant progress did not occur until the temperature was increased to 100°C. Although identification of the product was not achieved, the ^{1}H NMR spectrum was not consistent with that expected from compound **167**. Further purification of the product on a flash silica column resulted in decomposition and/or rearrangement.



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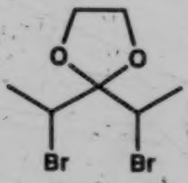

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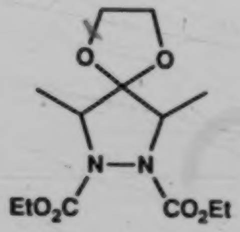
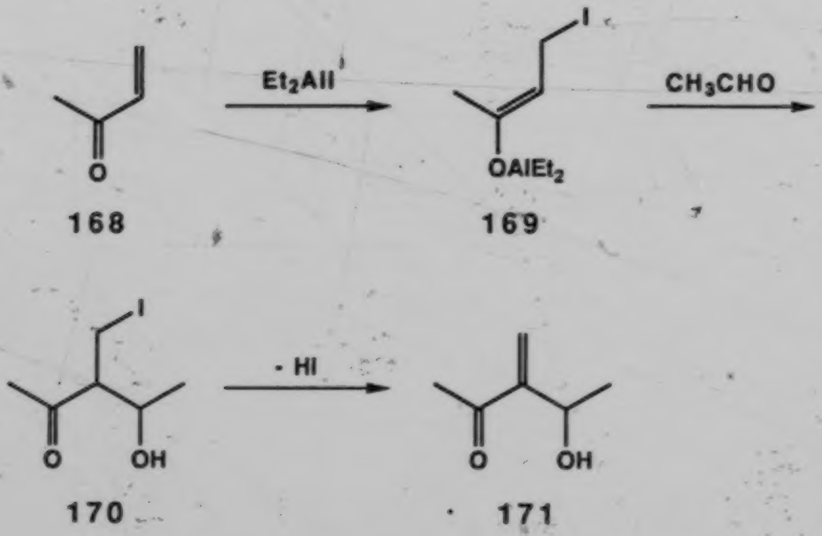


167

A repetition of the above procedure in the presence of sodium iodide produced a mild increase in reactivity, however the product obtained at 50°C was identical to that produced previously. The replacement of the nucleophile with the less bulky hydrazine (in ethanol) was also unsuccessful with or without the aid of sodium iodide. Refluxing for several days produced only starting materials as indicated by TLC and ^{1}H NMR. In another experiment the addition of potassium hydroxide to the hydrazine reaction mixture led to some reaction and the same undesired product.

Itoh *et al.* has reported[57] the synthesis of 4-hydroxy-3-methylene-2-pentanone **171** 61% yield from methyl vinyl ketone and acetaldehyde aided with diethyl aluminum iodide in (Eq. 38). Preferential 1,2 reduction would then have produced the desired 3-methylene-2,4-pentanediol **142**. The addition of diethyl aluminum iodide to a mixture of methyl vinyl ketone and acetaldehyde at 0°C followed by workup with acid, as indicated in the literature did not appear to generate any **171**. Adding acetaldehyde to a 0°C solution containing the other two components followed by acidic workup produced approximately 7% of product. The reaction of diethyl aluminum iodide and methyl vinyl ketone at -78°C, a temperature which might prevent undesired reactions of starting materials and intermediates, followed by the addition of acetaldehyde and acidic workup did not produce any product. The addition of DBU to assist the elimination of hydrogen iodide from intermediate **170** did not enhance the yield.

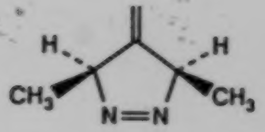


(Eq. 38)

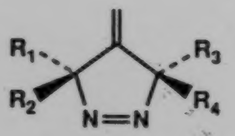
RESULTS

Diastereomeric Product Analysis

The diastereomeric purity of samples of *cis* and *trans*-3,5-dimethyl-4-methylene-1-pyrazolines (**125** and **126** respectively) was determined with baseline resolution on a 12 m x 0.20 mm i.d. methyl silicone fused silica capillary column. With the oven at 35°C and a linear helium flow rate of approximately 20 cm/min (zero retention time determined by methane gas injection) retention times for **126**, **125**, and E-3-methyl-4-ethylidene-1-pyrazoline **172** were 3.02, 3.14, and 4.14 minutes respectively. Since neither of the *cis* or *trans*-3,5-dimethyl-4-methylene-1-pyrazoline samples contained **172**, a separately synthesized authentic sample[36] was used to determine the retention time for **172**. Low resolution GC-MS verified that all three peaks had the correct mass of 110.

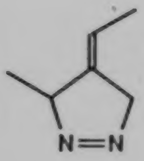


125



$R_1, R_4 = CH_3; R_2, R_3 = H$ or
$R_1, R_4 = H; R_2, R_3 = CH_3$

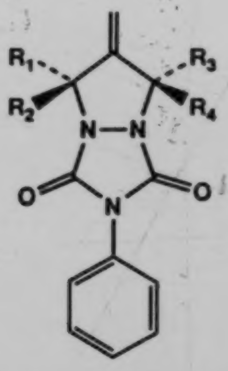
126



172

It was not possible to distinguish between *cis* and *trans*-3,5-dimethyl-4-methylene-1-pyrazoline (**125** and **126**) using their 400 MHz ^{1}H-NMR spectra. The structural assignment was achieved using other methods.

Positive identification of *trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione **144b** was established by its X-ray structure (Figure 1). Subsequent reaction steps maintained the



a) $R_2, R_4 = CH_3$; $R_1, R_3 = H$
b) $R_1, R_4 = CH_3$; $R_2, R_3 = H$ or
$R_1, R_4 = H$; $R_2, R_3 = CH_3$

144

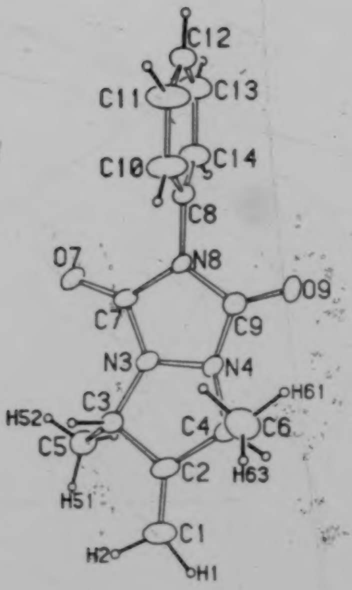
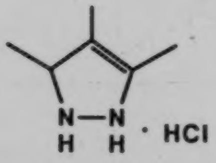


Figure 1 X-ray structure of **144b**

integrity of the allylic centers to produce the resulting pyrazoline, i.e., *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126**. Had epimerization of the allylic centers occurred during any of the reactions it would have been detected by ^{1}H-NMR spectra since **174** is thermodynamically more stable than **125** or **126** and **173** is thermodynamically more stable than **145.** In agreement, isomerically pure **144b** and **144a** produced different isomerically pure 3,5-dimethyl-4-methylene-1-pyrazoline isomers. Optically active **144b** generated an optically active pyrazoline **126**.



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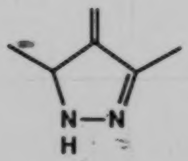
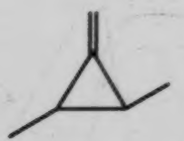


174

Since alkylidenecyclopropanes **131** - **134** are known to slowly isomerize at 170°C[36] an extrapolation to "0" time from a series of time staggered thermolysis samples was necessary. For both the *cis* and *trans* pyrazolines **125** and **126** approximately 4 mg of pyrazoline was dissolved in 250 µl of HPLC grade heptane. Both solutions were spiked with approximately 1 mg of deuterated benzene as an internal standard in order to estimate rate constants. The 250 µl were then split into 5 samples each (thus maintaining a constant pyrazoline/benzene ratio) and were then vapor transferred into ~16 ml breakseals. The samples were thermolyzed up to 40 minutes at 170.0 ± 0.1°C. The internal pressure in the breakseals was ~0.8-1.0 atmospheres. Each sample was quickly cooled in an ice-water bath and vapor transferred into traps. Complete transfer into and out of the break-



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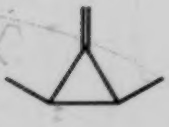

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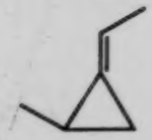

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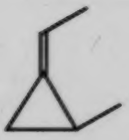


134

seals was guaranteed by transferring the samples till the vacuum apparatus reached the original <1 micron of pressure.

Quantitative analysis of the alkylidenecyclopropanes **131** - **134**, the deuterated benzene, and unreacted pyrazolines was accomplished on a 12 m x 0.20 mm i.d. methyl silicone column. It was necessary to decrease the oven temperature to -20°C in order to get baseline separation between E-2-methylethylidenecyclopropane **133** and Z-2-methylethylidenecyclopropane **134**. Identification of the alkylidenecyclopropanes was achieved by the analysis of a thermolysed sample of E-3-methyl-4-ethylidene-1-pyrazoline **172** of known[36] alkylidenecyclopropane proportions. At -20°C the retention times for the authentic alkylidenecyclopropane sample and products from the thermolysis of the pyrazolines **125** and **126** matched closely. A mixture of the authentic alkylidenecyclopropane sample and the product alkylidenecyclopropanes produced only the four expected peaks as can be seen in Figure 2.

A quantitative analysis of unreacted pyrazoline and deuterated benzene for each set of 5 samples was made at 35°C using the same conditions as the initial pyrazoline analysis. The deuterated benzene had a retention time of 7.1 minutes and was baseline resolved.

All errors listed in quantitative measurements and calculations are one standard deviation (SD) of the mean.

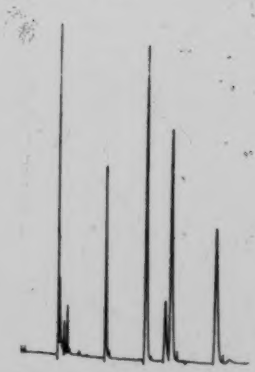


Figure 2 Product alkylidenecyclopropanes spiked with an authentic sample

Thermolysis of *cis*-3,5-Dimethyl-4-methylene-1-pyrazoline 125

The initial thermolysis sample had a composition of 98.1 ± 0.1% *cis* pyrazoline **125** and 2.0 ± 0.1 % *trans* pyrazoline **126**. Final alkylidenecyclopropane compositions (average of 3-4 runs) for thermolysis at 170°C for 5,10,20, and 40 minutes are listed in Table 11 and plotted in Figure 3. The non-horizontal slope of % alkylidenecyclopropane vs time shows that a very slow isomerization of the alkylidenecyclopropanes does occur. The rates of these alkylidenecyclopropane isomerizations have been studied by Gajewski and Chou[35]. Initial alkylidenecyclopropane composition without isomerization (Table 11) was estimated by a weighted linear least squares fit of the data and extrapolation to "0" time. The composition data listed in Table 11 and plotted in Figure 3 are not corrected for the initial 2.0 % of *trans* pyrazoline isomer **126**. The actual product composition for pure *cis* pyrazoline **125** thermolysis could vary as much as 0.2 % for Z-2-methyl ethylidenecyclopopane **134** to 0.6 % for *cis*-2,3-dimethylmethylenecyclopropane **132**.

Thermolysis of cis–3,5–Dimethyl–4–methylene–
1–pyrazoline at 170°C.

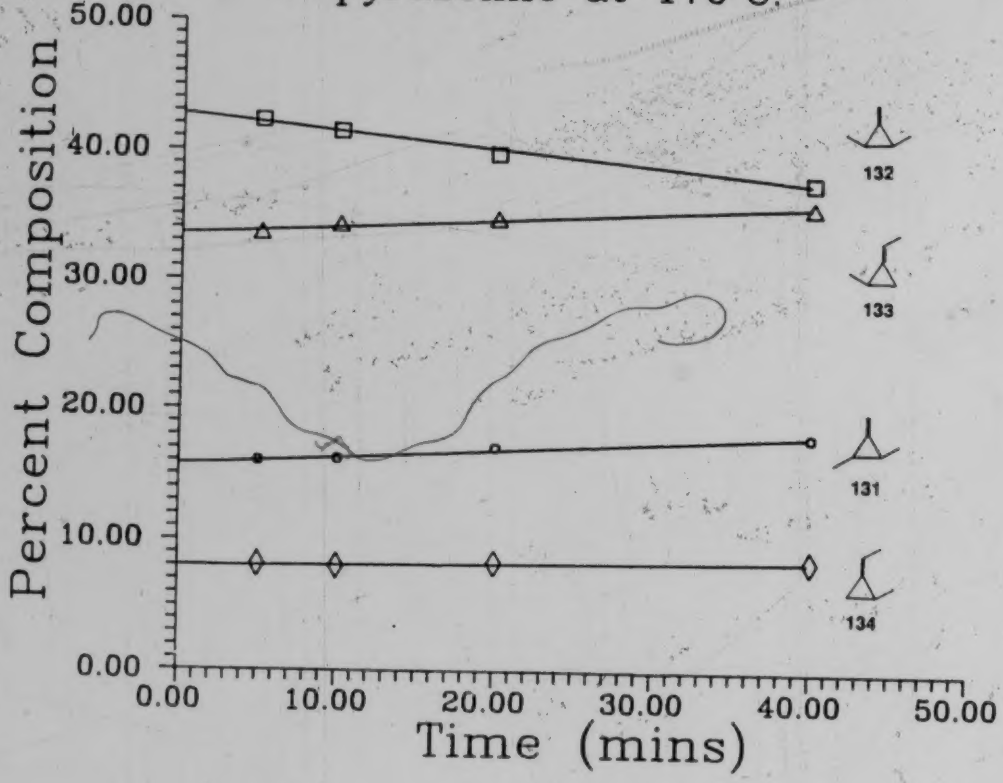
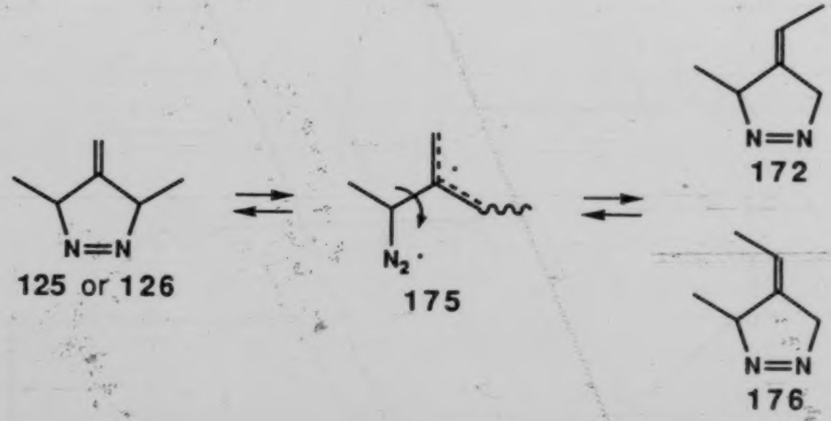


Figure 3

There was no evidence of isomeric **172** or **176** being produced during the reaction as would be expected if one bond reversible cleavage had occured (Scheme 14).

The presence of the internal standard benzene-d_6 permitted Eq. 39 to be used to estimate a first order rate constant for the thermolysis of the *cis* pyrazoline **125.** A plot of the data in Table 15 was reasonably linear and indicated a first order rate constant of $1.66 \pm 0.15 \times 10^{-3}$ sec^{-1}. From the rate constant a half life of 7.0 minutes was calculated thus the kinetics and product alkylidenecyclopropane composition was followed over a period of ~6 half lives.



Scheme 14

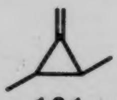
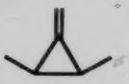
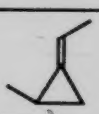
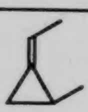
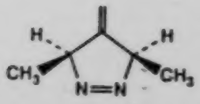
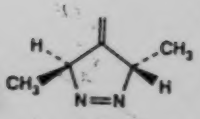
$$-\ln\left(\frac{[\text{pyrazoline}]_f}{[\text{pyrazoline}]_i}\right) = kt$$

(Eq. 39)

Thermolysis of *trans*-3,5-Dimethyl-4-methylene-1-pyrazoline 126

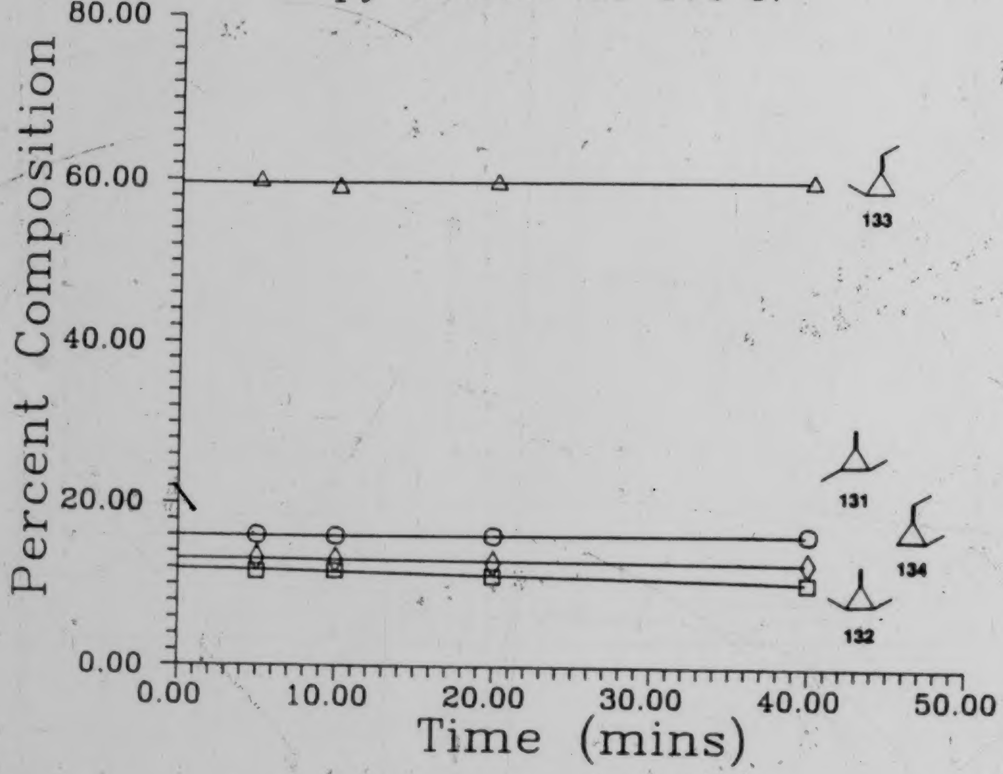
The initial thermolysis mixture consisted of >99.8% *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126.** Final thermolysis (170.0°C) alkylidenecyclopropane compositions are listed in Table 11. A plot of the alkylidenecyclopropane composition vs time is shown in Figure 4. Similar to the product behavior from the *cis* pyrazoline thermolysis, slow isomerization of the alkylidenecyclopropanes occurred, thus an extrapolation of a weighted least squares fit of the data to "0" time was necessary in order to obtain initial product compositions without isomerizations (Table 11).

Table 11. Final alkylidenecyclopropane compositions and their "0" time extrapolations from the thermolysis of 3,5-dimethyl-4-methylene-1-pyrazolines 125 and 126 (170°C, 0.8-1.0 atm)

Reactant	Time (minutes)	Product Composition (%)			
		 131	 132	 133	 134
 125	40.0	18.0 ± 0.3	37.7 ± 0.3	35.8 ± 0.2	8.5 ± 0.3
	20.0	17.1 ± 0.2	39.8 ± 0.5	34.8 ± 0.5	8.3 ± 0.3
	10.0	16.2 ± 0.3	41.5 ± 0.1	34.3 ± 0.3	8.0 ± 0.2
	5.0	16.0 ± 0.2	42.3 ± 0.4	33.6 ± 0.2	8.1 ± 0.5
	0[a]	15.8 ± 0.2	42.8 ± 0.2	33.4 ± 0.2	7.8 ± 0.1
 126	40.0	16.4 ± 0.3	10.4 ±0.9	60.4 ± 0.9	12.8 ± 0.5
	20.0	16.1 ± 0.6	11.1 ± 1.0	60.1 ± 1.0	12.7 ± 0.8
	10.0	16.0 ± 0.5	11.7 ± 0.6	59.3 ± 0.8	13.0 ± 1.0
	5.0	16.0 ± 0.9	11.5 ± 1.2	60.0 ± 1.2	13.1 ± 1.2
	0[a]	15.9 ± 0.1	12.0 ± 0.2	59.4 ± 0.4	12.7 ± 0.2
	∞[b]	6.2	2.5	47.8	43.8

[a] Zero time value obtained by extrapolation.

[b] Equilibrium value,see reference 58.



Thermolysis of trans-3,5-Dimethyl-4-methylene-1-pyrazoline at 170°C.

Figure 4

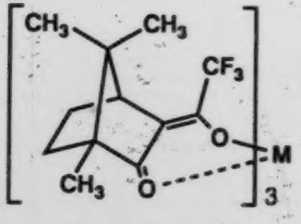
The presence of the internal standard benzene-d_6 permitted Eq. 39 to be used to estimate a first order rate constant for the thermolysis of the *trans* pyrazoline **126.** A plot of the data in Table 11 was reasonably linear and indicated a first order rate constant of $2.03 \pm 0.07 \times 10^{-3}$ sec^{-1}. From the rate constant a half life of 5.7 minutes was calculated, thus the kinetics and product alkylidenecyclopropane composition was followed over a period of ~7 half lives.

As can be seen from the rate constants determined from Tables 17 and 18, the *trans* pyrazoline **126** reacts 20% faster than the *cis* pyrazoline **125**. Thus if the rate determining one-bond homolysis step was reversible, formation of the *cis* pyrazoline **125** and/or 3-methyl-4-ethylidene-1-pyrazolines **172** or **176** should occur when starting from pure *trans* pyrazoline **126** (Scheme 14). Samples thermolysed and quenched before reaction completion showed no evidence of **125** or **172** and **176** therefore reversibility is unlikely.

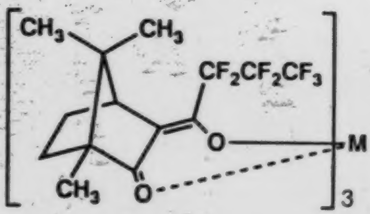
Enantiomeric Product Analysis

Determination of the Enantiomeric Purity of *trans*-3,5-Dimethyl-4-methylene-1-pyrazoline 126

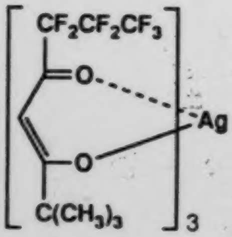
Ideally, in order to be the most precise in an enantiomeric study of the thermolysis products of chiral *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126**, a direct measurement of the enantiomeric purity of the pyrazoline should be made. These compounds, however, tend to tautomerize to structure **174** in the presence of acid and base particularly at temperatures greater than 25°C, thus restricting possible resolution techniques. A search for an appropriate commercially available chiral capillary column was fruitless. Since pyrazoline **126** proved to be stable to lanthenide and binuclear lanthenide-silver NMR shift reagents, the chiral lanthenide shift reagents **177-178a** and combinations of these shift reagents with silver compounds **178b** and **179** in $CDCl_3$ were tried. Binuclear shift reagents have the advantage[59,60] of being able to coordinate with soft lewis bases such as olefins while lanthenide shift reagents alone coordinate with harder lewis bases. Complexation of the shift reagents with the nitrogens or the olefin of **126** resulted, at best, in only a small net shift in the 400 MHz ^1H NMR spectra of racemic **126**.



a) M = Eu
b) M = Yb
177



a) M = Yb, Pr
b) M = Ag
178



179

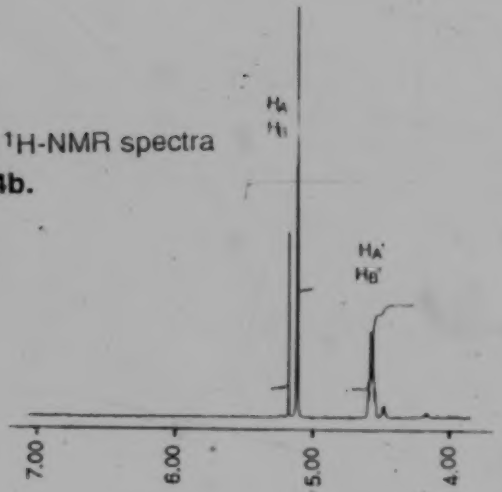
It was possible, however, to determine the the enantiomeric purity of *trans*-5,7-dimethyl-6-methylene-2-phenyl-[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione **144b** using the lanthenide shift reagent (+)-Eu(facam)$_3$ **177a**. The chemical shifts of

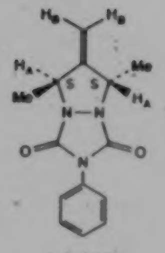
(+)-Eu(facam)$_3$ **177a**. The chemical shifts of various (±)-**144b** protons were tracked through a series of 400 MHz ^{1}H-NMR spectra of 5-8 mg of dione in CDCl$_3$ containing successive additions of shift reagent dissolved in CDCl$_3$. The only useful protons for integration were those attached to the allylic carbons and those on the exocyclic methylene with the former giving the best separation of the protons of (±)-**144b**. Upfield from 4 ppm shift reagent absorbances superimposed on the (±)-**144b** peaks, while the aromatic protons were insufficiently separated. The best resolution of the protons from the (±)-**144b** without excessive broadening of the peaks occured at an approximate 1:1 ratio of shift reagent:**144b** (Figure 6). In this figure H_A and H_B identify the previously enantiomeric protons of a near racemic (±)-**144b**. Figure 5 shows a partial 400 MHz ^{1}H-NMR spectrum of the (+)-**144b** that was used as a precursor to the product study for the thermolysis of chiral 3,5-dimethyl-4-methylene-1-pyrazoline **126**. This sample contained 11.1 ± 2 0 % of the *cis* isomer **125**. Enantiomeric purity of the sample in Figure 5 was determined by the 400 MHz spectrum in Figure 7. This sample contained approximately a 1:1 mixture of shift reagent:(+)-**144b**. The integration of the proton signals represents an average of 9006 scans. Although no pulse delay was used after an acquisition period the integral should be reasonably accurate since the presence of the paramagnetic shift reagent would lead to rapid spin relaxation. From Figure 7 H_A and H_B can be identified as belonging to (+)-**144b** while H_A' and H_B' are from (-)-**144b**. The integral in Figure 7 indicates that the sample contained a 93.4 ± 2.0 % enantiomeric excess (ee) of (+)-**144b** (i.e.,96.7 % (+)-**144b**, 3.3 % (-)-**144b**).

A 3.7 mg sample of the (+)-**144b** had an observed optical rotation of +0.104 ± 0.002° when measured in a 1.000 dm cell at 22°C and 589 nm.

Figure 5

400 MHz ^{1}H-NMR spectra of (+)-**144b.**

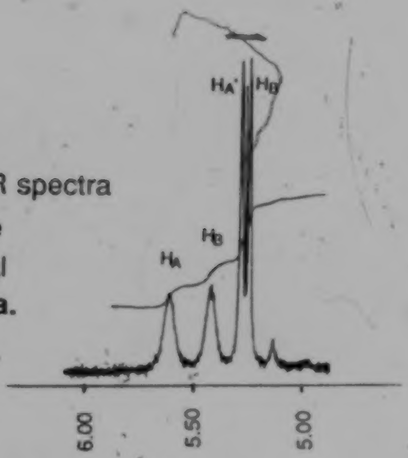


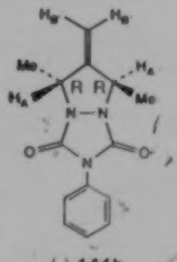


(+)-144b

Figure 6

400 MHz ^{1}H-NMR spectra of (±)-**144b** in the presence of chiral shift reagent **177a.**

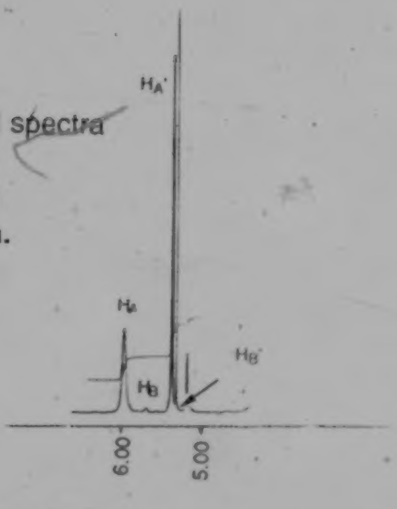




(-)-144b

Figure 7

400 MHz ^{1}H-NMR spectra of (+)-**144b** in the presence of chiral shift reagent **177a.**



After taking into account the 11.1 ± 2.0 % of *cis* isomer **144a,** Eq. 40 was used to determine the specific rotation of the diastereomerically pure but optically impure (+)-**144b** sample (93.4 ± 2.0 % ee), $[\alpha]^{22}D = 31.9 \pm 2.3°$ ($CHCl_3$). Using the same equation diastereomerically and optically pure (+)-**144b** should have rotation, $[\alpha]^{22}D = +34.2 \pm 3.4°$ ($CHCl_3$).

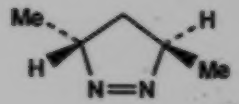
$$[\alpha] = \frac{\alpha}{lc}$$

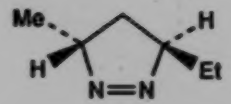
$[\alpha]$ = specific rotation
α = observed rotation
l = cell length in dm
c = concentration in g/ml

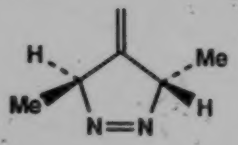
(Eq. 40)

The (+)-**144b** sample was then hydrolyzed and acidified to the *trans*-hydrochloride **145b** which was then oxidized with benzene selenenic anhydride to optically active (-)-*trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126**. As was discussed previously there was no indication of any *cis/trans* isomerization during this reaction sequence thus it is highly unlikely that any loss of enantiomeric purity occured through the formation of intermediates such as **173** and **174**. GC analysis (3 runs) indicated that the pyrazoline generated consisted of 95.9 ± 0.3 *trans* isomer and 4.1 ± 0.2 *cis* isomer.

Mishra and Crawford[61] have assigned a 3R:5R configuration to (+)-*trans*-3,5-dimethyl-1-pyrazoline **146**. Similarily Bergman *et al.*[62] have assigned a 3R:5R configuration to (+)-*trans*-3-ethyl-5-methyl-1-pyrazoline **181**. The analogous (-)-*trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126a** should have a 3S:5S configuration since the additional olefin function, which is perpendicular to the primary diazo chromophore, should not influence the rotational direction[63]. Its precurser triazoline dione (+)-**144b** would thus have a 5S:3S configuration. Verification of this was achieved by x-ray crystallography (see Appendix C).


146


181


126a

An estimate of the specific rotation of optically pure pyrazoline **126** was determined from a sample generated from (-)-*trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine1,3-dione **144b** with an ee of 83.4 ± 2.0 %. The pyrazoline sample (11.3 mg/ml, α^{22} D = +3.30, 10.000 cm cell, 22°C) was diastereomerically pure but contained 2.3 % CH_2Cl_2 and 7.6 % other impurities by capillary GC analysis (methyl silicone column). Since the impurities had retention times less than that of the pyrazoline their molecular weight was estimated to be <120 g/mole. Taking into account the impurities Eq. 40 determined that optically pure (+)-**126** had rotation, $[\alpha]^{22}$D = +376 ± 30° (CCl_4).

Product Alkylidenecyclopropane Separation and Analysis from the Thermolysis of Optically Active (+)-*trans*-3,5-Dimethyl-4-methylene-1-pyrazoline 126

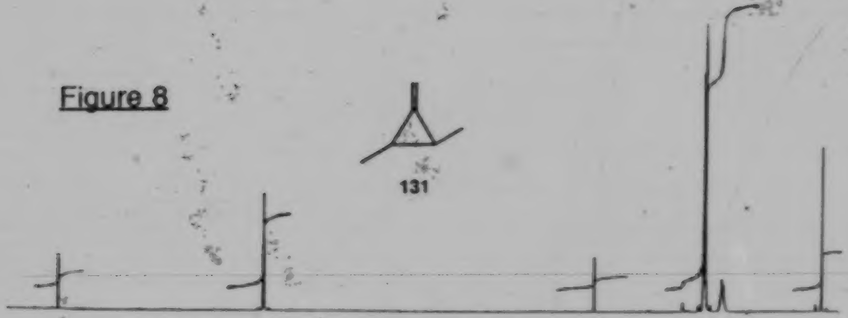
Two ~45 mg samples of the above mixture were thermolysed in 16 ml breakseals for 15.0 minutes at 170.0 ± 0.1°C using techniques described previously. A maximum pressure of 2.0 atm. was possible at 100 % reaction.

The trapped alkylidenecyclopropanes were dissolved in 200 μl of toluene. Preparative separation of the alkylidenecyclopropanes was achieved on a 18.3 m x 6.4 mm aluminum column packed with 20 % dimethylsulfolane on Chromosorb Paw[36]. Column temp, 30°C. Injector temp, 150°C. TCD, 100°C. Sample size, 50 μl. Helium flow rate, 30 ml/minute. Retention times were (minutes): *trans*-2,3-dimethylmethylenecyclopropane **131** (75), *cis*-2,3-dimethylmethylenecyclopropane **132** (121), E-2-methylethylidenecyclopropane **133** (131), and Z-2-methylethylidenecyclopropane **134** (137). The alkylidenecyclopropanes were trapped in a pre-dryed glass coil immersed in liquid nitrogen. The coil was equipped with high vacuum stopcocks to prevent the accumulation of moisture when the GC helium purge was not present. Samples were then vacuum transferred to a tared 1 ml volumetric flask. The flask was reweighed and filled to a 1 ml volume with CCl_4. Control runs indicated that weight increases in the tared flask after the trapping and transferring processes were negligible. Optical rotations of alkylidenecyclopropanes **131-134** were measured over a range of wavelengths from 589-365 nm on two separate polarimeters. Taking solvent rotation into account the largest rotations were observed for isolated **133** with values of -0.001° at 589 nm and -0.003° at 365 nm. Since the polarimeters had an accuracy of ±0.002° and a reproducibility of <0.002° it was estimated that a rotation of ±0.003° at 589 nm would positively indicate optical activity in the sample measured; no optical activity was found in any of the alkylidenecyclopropanes **131**, **133**, and **134**.

Analysis of the CCl_4 solutions by capillary GC (methyl silicone column) indicated that all samples contained <2 % of materials other than alkylidenecyclopropanes and that the *trans*-2,3-dimethylmethylenecyclopropane **131** was isomerically pure. Since separation of the E and Z isomers (**133** and **134** respectively) was difficult due to an effect of the CCl_4 solvent used 400 MHz ^{1}H-NMR spectra (Figure 8-10) were used to determine their diastereomeric purity. The spectra indicate that all three samples were diastereomerically pure, however **131** and **133** may have had up to 5 % impurities while **134** up to 10 % impurities. Attempts were made to separate the 400 MHz ^{1}H-NMR signals of the enantiomers present in a mixture of racemic alkylidenecyclopropanes **131-134** by using binuclear chiral lanthanide shift reagents. Various combinations of lanthanide shift reagents **177-178a** with silver compounds **178b** and **179** provided insufficient resolution.

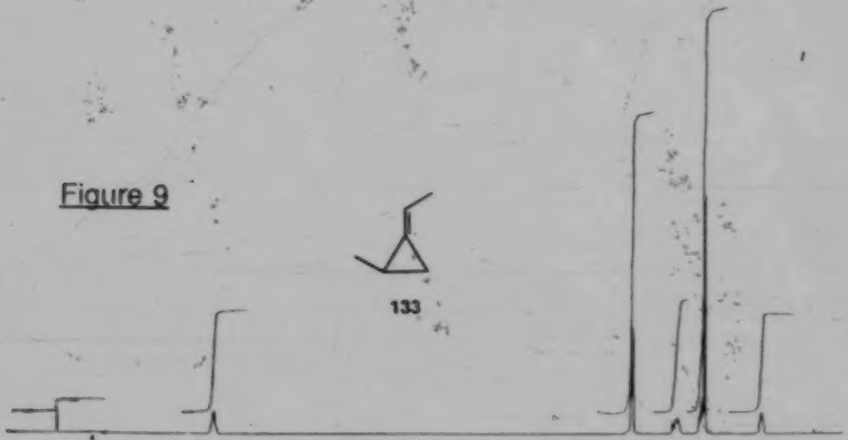
Polarimetry was therefore used to determine the enantiomeric purity of MCP **131**,**133**, and **134**. Gajewski[63] has made *trans*-2,3-dimethylmethylenecyclopropane **131a**; $[\alpha]^{22}D = -59.4°$ (CCl_4). Although the sample used for this measurement was not necessarily optically pure (~85% pure) its value was used to determine the maximum possible enantiomeric excess (ee) obtained in the recovered *trans*-2,3-dimethylmethylenecyclopropane **131** from an optically pure pyrazoline **126**. After correcting for the 4.11 ± 0.20 % of *cis* pyrazoline isomer **125**, the 93.4 ± 2.0 % ee of the optical isomer of **126** used, and the minimum purity of 95 %, the amount of optically pure MCP **131** used for the rotational measurement was calculated to be 2.65 mg. Eq. 40 and the minimum rotation that would indicate definate optical activity in the product (0.003°) were then used to determine the minimum amount of optically pure pyrazoline **126** that generated optically active **131**. The calculated maximum possible ee in **131** was 1.9 ± 0.2%. Since the reference sample used was ~85% pure

Figure 8


131

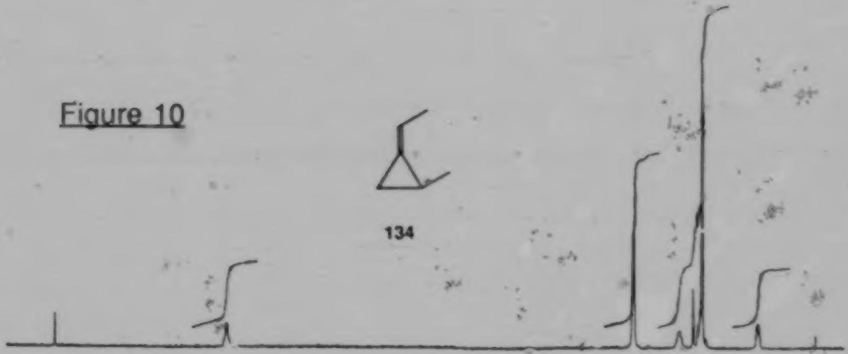
400 MHz ^{1}H-NMR spectra of **131.**

Figure 9


133

400 MHz ^{1}H-NMR spectra of **133.**

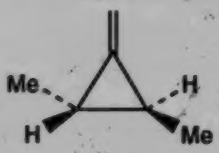
Figure 10


134

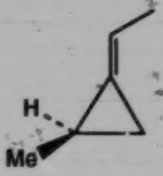
400 MHz ^{1}H-NMR spectra of **134.**

<2.0% of optically pure **126** led to optically active *trans*-2,3-dimethylmethylenecyclopropane **131**.

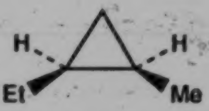
Gajewski[63] has also isolated E-2-methylethylidenecyclopropane **133b**, $[\alpha]^{22}D = +10.7 \pm 1.0°$ (CCl_4). Hydrogenation of this sample over a platinum catalyst produced *cis*-1-ethyl-2-methylcyclopropane **180**, $[\alpha]^{22}D = -12.8 \pm 4.0°$ (CCl_4). Since Bergman[64] has determined that the maximum specific rotation of **180** at -16.2°, the maximum specific rotation of **133b** can be estimated at $[\alpha]^{22}D = +15.2 \pm 4.8°$. Using the same arguments presented previously, a calculated maximum possible ee of MCP **133** of 3.2 ± 1.2% means that <5% of optically pure pyrazoline **126** produced optically active alkylidenecyclopropane **133**. A similar analysis of the minimum observable rotation of Z-2-methylethylidenecyclopropane **134** could not be made since an estimate of the rotation of optically pure **134** was not available. However if the maximum rotation of **134** is similar to that of **133** an enantiomeric excess of 10% should have been detected.



131a



133b

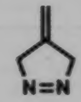
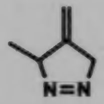
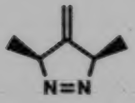
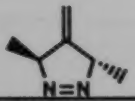


180

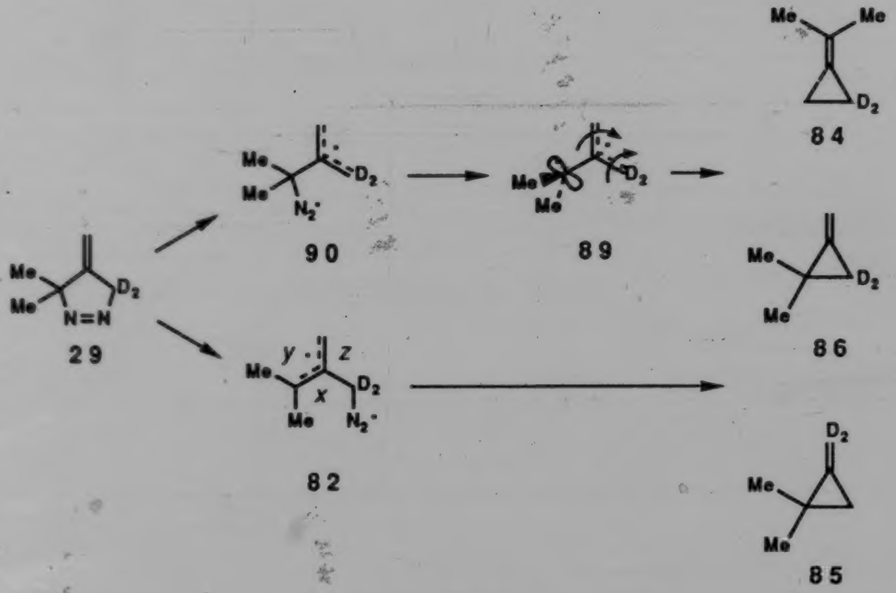
DISCUSSION

A complete understanding of the thermolysis mechanism of 4-alkylidene-1-pyrazolines to produce alkylidenecyclopropanes has been and is difficult to attain. An attempt was made initially to find a mechanism common to the entire family of 4-alkylidene-1-pyrazolines; however variations in substituents appears to lead to a range of mechanisms. Nevertheless, certain aspects of the thermolysis mechanism can be expected to be transferable within the entire family. The majority of evidence indicates that the thermolysis of 4-alkylidene-1-pyrazolines involves a minimum of two steps, the first of which is a rate-determining one-bond homolysis of a C-N bond. A discussion of the first step is presented in the introduction of this thesis. The estimated first order rate constants for the thermolysis of *cis* **125** and *trans*-3,5-dimethyl-4-methylene-1-pyrazolines **126** at 170°C are $1.66 \pm 0.15 \times 10^{-3}$ and $2.03 \pm 0.07 \times 10^{-3}$ respectively. These rates compare favorably with the thermolysis of the 4-alkylidene-1-pyrazolines in Table 12, thus a deviation from a one-bond homolysis is not expected. The trend towards minor rate enhancements from the unsubstituted parent **1** to the mono-methyl **21** to the C_3 and C_5 dimethyl **125** and **126** is consistent with the increasing stability of the developing alkyl radical. A comparison of the KIE (Table 2) of **29** (1.18 ± 0.03) and **32** (1.02 ± 0.02) suggest that cleavage of the methyl substituted C_3-N bond of **21** is minor. Both **125** and **126** have kinetically equivalent C-N bonds and have a methyl substituent on each carbon and would therefore lead to a larger rate enhancement. Little change in rate is noted (Table 12) and ground state conformational factors may explain what little differences there are.

Table 12 Rates at 170°C for some 4-methylene-1-pyrazolines

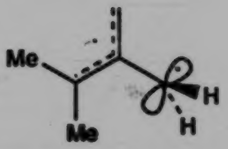
	Compound	k x 10^3 (170°C) (s^{-1})	Rel. Rate	Ref
1		1.45 ± 0.01	1.00	17
21		1.51 ± 0.03	1.04	24
125		1.66 ± 0.15	1.14	this work
126		2.03 ± 0.07	1.40	this work

Major deviations within the family of 4-alkylidene-1-pyrazolines occur in the product determining step. As was discussed in the introduction Crawford *et al.*[5,17,18] were able to algebraically rationalize and/or accurately predict product proportions derived from the thermolysis of 4-alkylidene-1-pyrazolines with primary or tertiary allylic endocyclic carbons, specifically compounds **29**, **27**, **33**, **34**, **36**, and **53** (see Schemes 8, 7, and 6). As an example of both primary and tertiary systems[5], the thermolysis of **33** via a one-bond homolysis would initially produce the diazenyl radicals **90** and **82** (Scheme 15). Because of the ease of formation of the tertiary radical, the lifetime of intermediate **90** would be expected to be short , thus producing the Chesick diradical **89**. The diazenyl radical **82**, on the other hand, would be expected to have a longer lifetime since loss of nitrogen would produce the less stable primary Chesick diradical **66**. Following least motion principals[33] the Chesick diradical **89** would form products by the rotation of either of the allylic termini to form a ring sigma bond between the rotating allylic "p" orbital and the orthogonal orbital. Rotation of the two allylic termini to form a product ring sigma bond would not be expected since three orbitals would have to rotate (see **182**). The formation of products from the diazenyl radical **82** would occur by rotation of either of the allylic termini and backside displacement of nitrogen to form an endocyclic sigma bond (*x* and *z* mode) and by rotation of the two allylic termini to form an endocyclic sigma bond probably with synchronous loss of nitrogen (*y* mode). Utilizing this type of intermediate behavior Crawford *et al.*[5] were able to predict final product proportions of 15:44:41 for **84**:**86**:**85**. The observed values are 16:44:40.

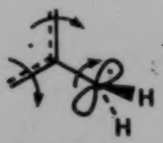


Scheme 15

The key to the success of the above analysis appears to be linked to the lifetime of the diazenyl radical(s) produced by one-bond homolysis of

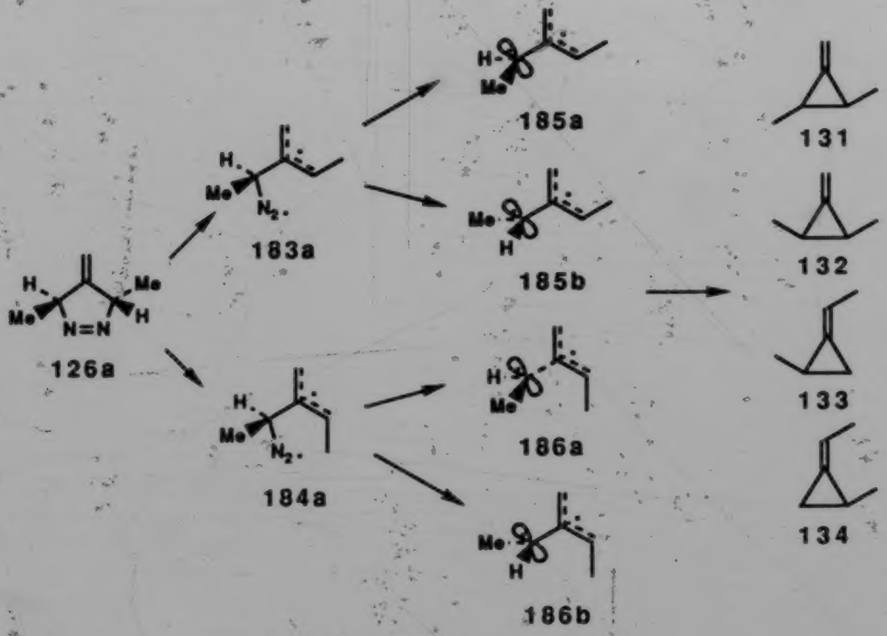


66



182

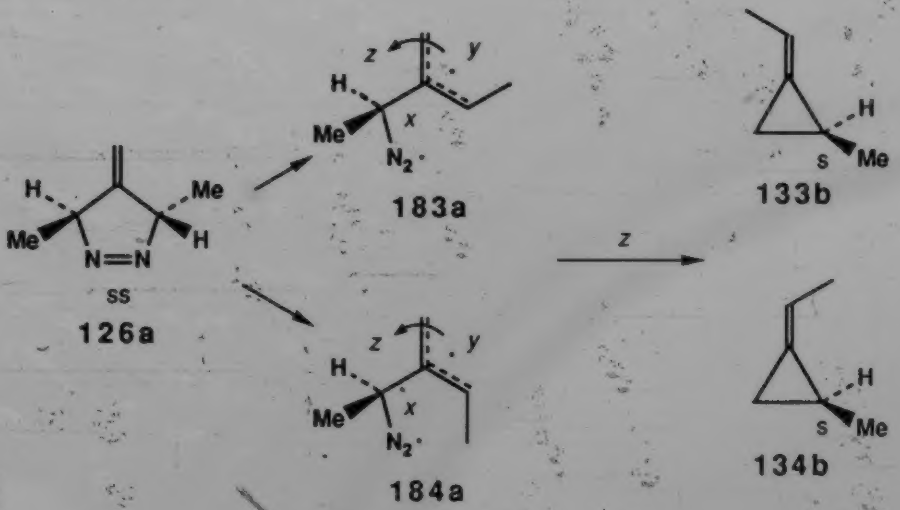
the two possible C-N bonds. In the previous case the two extremes are met by the formation of primary and tertiary diazenyl radicals. Since the thermolysis of 4-alkylidene-1-pyrazolines with secondary allylic endocyclic carbons would produce diazenyl radicals whose stability falls between the two extremes, there is an ambiguity as to whether products are formed from diazenyl radicals, Chesick diradicals or a mixture of the two. For this reason we have studied the thermolysis of optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126** (Scheme 16). One-bond homolysis of either one of the two kinetically equivalent C-N bonds could produce two chiral diazenyl radical intermediates **183a** and **184a** differing by a 180° rotation of the planar allylic ethylidene group. Depending on the rotation of the diazenyl group loss of nitrogen could form four Chesick diradical isomers **185a**, **185b**, and **186a**, **186b** in which **185** and **186** represent a diastereomeric pair of enantiomers. Product formation via the diazenyl radicals and/or the Chesick diradicals could then produce four diastereomeric products **131**, **132**, **133**, and **134** in which **131**, **133**, and **134** each represent a pair of enantiomers. For the clarity of this discussion the 3S,5S configuration is assigned to the optically active pyrazoline **126** used in the discussion. Product formation resulting in an inversion of configuration at the chiral centers would then produce products with an S configuration while retention would produce products with an R configuration.



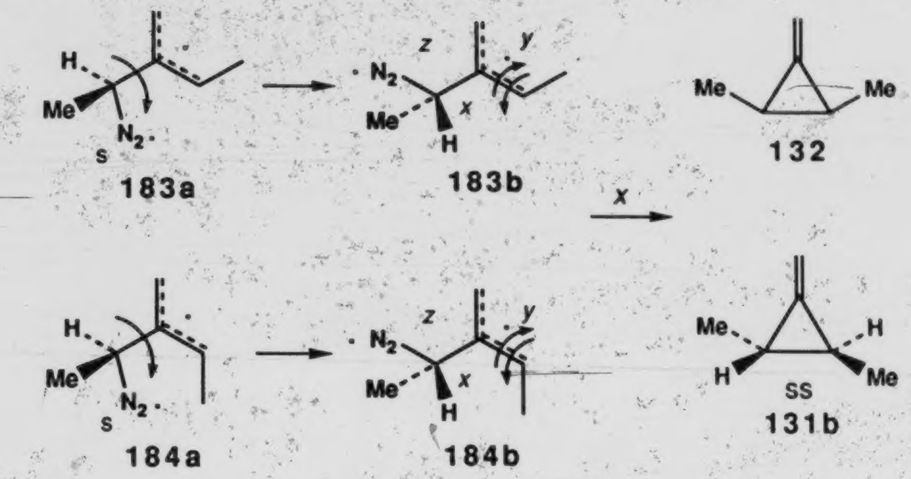
Scheme 16

Experimental results indicate that the thermolysis at 170°C of optically pure *trans* pyrazoline **126** produced optically inactive **131**, **133**, **134** and achiral **132**. It was estimated that <2% of enantiomeric excess in **131** and <5% of enantiomeric excess in **133** produced from optically pure pyrazoline **126** could have been detected with the polarimeters used. An estimate of the detectability of optical purity for **134** was not possible since an estimate of the rotation of optically pure **134** is not available, however if the maximum rotation of **134** is similar to that of **133** an enantiomeric excess of 10% should have been detected. These results virtually eliminate the possibility of alkylidenecyclopropanes being formed via diazenyl radical intermediates since backside displacement of **183a** or

184a nitrogen via the *z* mode in Scheme 17 would lead to inversion of stereochemistry at the chiral center and hence result in optical activity in ethylidenecyclopropanes **133b** and **134b**. Similarly C-C bond rotation by **183a** and **184a** to form diazenyl radicals **183b** and **184b** (Scheme 18) and methylenecyclopropane formation by backside displacement of nitrogen in the *x* mode would lead to achiral **132** and optically active **131b** with inversion of stereochemistry. It is also possible, though extremely unlikely, that all products are formed from *y* closure thus losing chiral information since the chiral center would become the products planar exocyclic ethylidene, however this would preclude the formation of any 2,3-dimethylmethylenecyclopropanes which are experimentally found to be 27.7 % of the products formed. Thus experimental results limit product formation from diazenyl radicals to <2 % via the *x* mode and <5 % via the *z* mode.

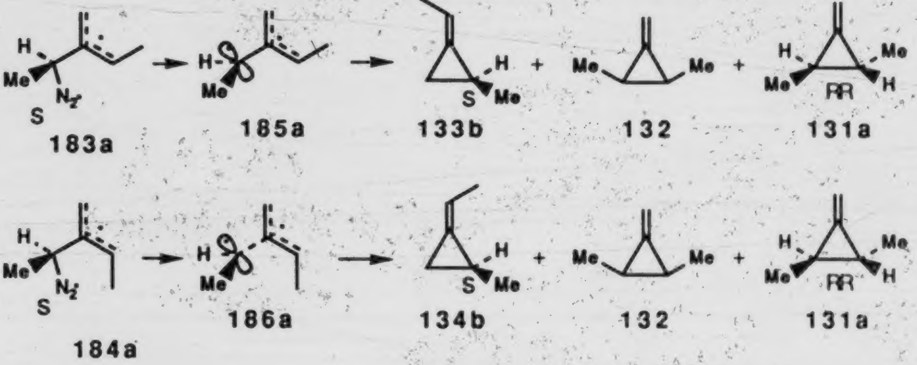


Scheme 17



Scheme 18

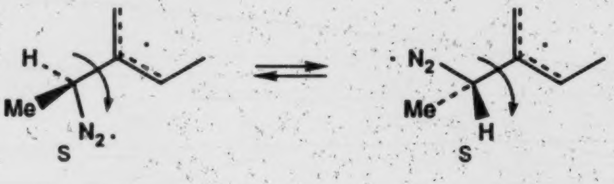
We therefore considered product formation from Chesick diradicals. In the event that nitrogen loss from diazenyl radicals from **183a** and **184a** is extremely rapid and rotation of the diazenyl bearing carbon does not occur, Chesick diradicals **185a** and **186a** would result (Scheme 19).



Scheme 19

Products formed by rotation of the methylene allylic terminus of **185a** and **186a** would generate **133b** and **134b** with net inversion of the chiral center, while rotation of the ethylidene allylic terminus would produce the achiral **132** and optically active **131a** with retention of configuration. Again the absence of optical activity in the products also limits this mechanism to <2% via ethylidene rotation and to <5% via methylene rotation.

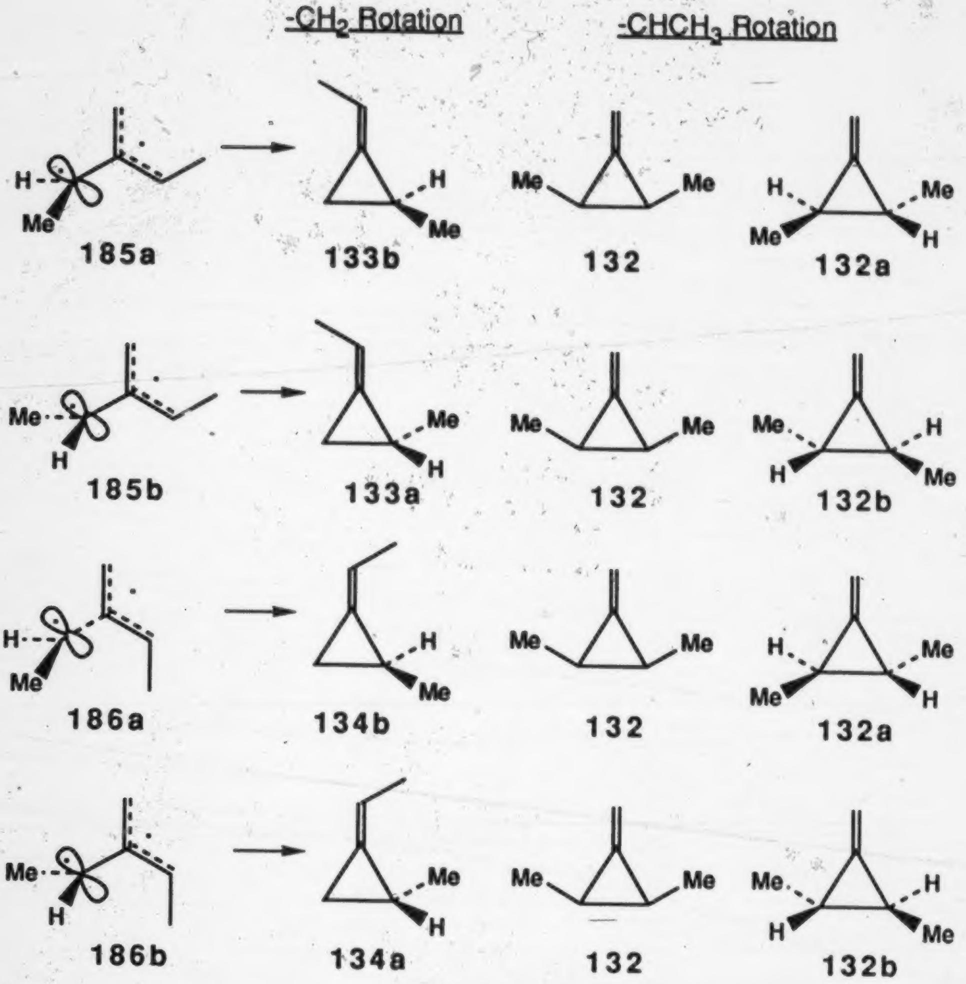
It is also possible that the diazenyl radical intermediates are stable enough to allow rotamer equilibration (Eq. 41) prior to loss of nitrogen. The equilibrated rotamers **183** and **184** would produce Chesick diradicals **185a**, **185b**,and **186a**, **186b** (Scheme 20) in which **185** and **186** are diastereomeric pairs of enantiomers, thus product formation produces enantiomeric pairs **133** and **134** via methylene rotation, and the enantiomeric pair **132** as well as the achiral **132** via ethylidene rotation.



183a **183b**

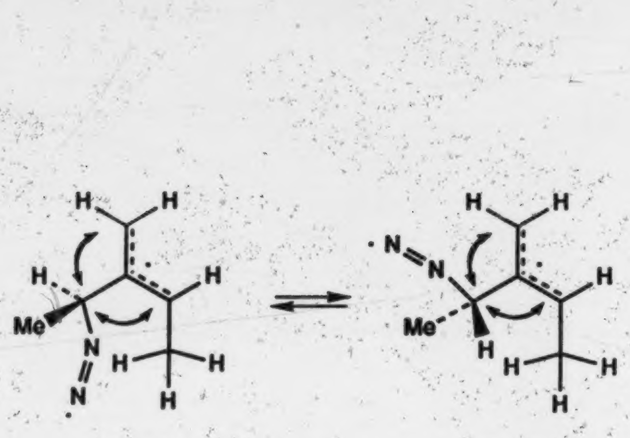
(Eq. 41)

Thus if enantiomeric Chesick diradicals **185a** and **185b** were formed in equal amounts and enantiomeric Chesick diradicals **186a** and **186b** were formed in equal amounts total racemization of the products would occur. It is unlikely that rotamers **184a** and **184b** (Eq. 42) would have equal populations since the steric bulk of the allylic termini are vastly different (CH_3 vs H), however, the allylic termini for the rotamers **183a** and **183b** (Eq. 43) would have a similar steric interaction with the bulky chiral center. Thus, if one-bond homolysis of optically active *trans* pyrazoline **126a** produces only the diazenyl radical rotamers **183** it is possible that rotamer



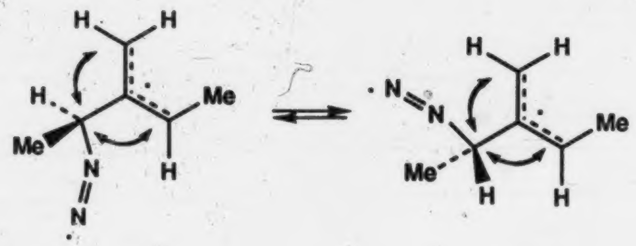
Scheme 20

equilibration and subsequent loss of nitrogen to form Chesick diradicals **185** could lead to racemic products. Principals of least motion and the interpretation of prior experimental evidence[5,29] leads one to predict that products will not be formed by sigma bond formation between the Chesick diradical allylic termini of **185**, thus any Z-2-methylethylidenecyclopropane **134** formed must be generated from the Chesick diradicals **186**. For the



184a **184b**

(Eq. 42)

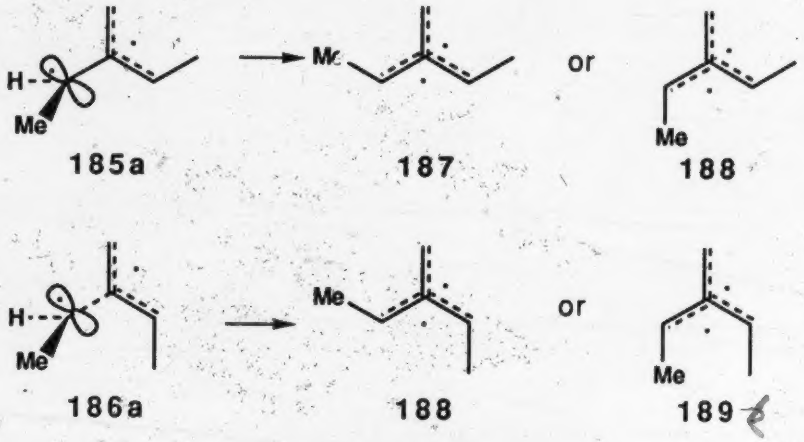


183a **183b**

(Eq. 43)

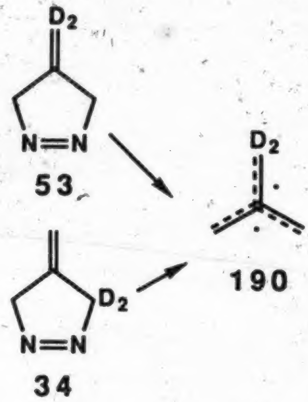
trans pyrazoline **126a** ethylidenecyclopropane **134** represents 12.7 % of the total alkylidenecyclopropanes generated thus the diazenyl radical **184** would have been formed in a minimum of 12.7 %. Conversely, since E-2-methylethylidenecyclopropane **133** is generated in 59.6% yield, the diazenyl radical **183** would have formed at least 59.6% of the time. Thus the diazenyl radical **184** , by this mechanism, is restricted to 13-40% of the total diazenyl radicals generated and is likely formed at ~26%. Nevertheless, since **134** was found to have no optical rotation, and if one assumes that a 10% enantiomeric excess could have been detected, the rotamer distribution between **184a** and **184b** would have been between 45:55 to 50:50. This minor difference in rotamer distribution would suggest that either the allylic H and CD_3 group are of similar size, or the tetrahedral diazenyl bearing carbon is nearly symmetrically substituted, or the interaction between the allylic termini and the chiral center is minimal. These explanations seem unlikely.

An alternative, and potentially attractive, explanation for the wide spread generation of racemic products involves the planarization of possible intermediate Chesick diradicals. The simplest planar intermediate possible for the thermolysis of **126a** are **187** and **189** which may be generated from Chesick diradical **185** and **186** respectively and **188** which may be generated from both (90° rotation of orthogonal group - Scheme 21). These



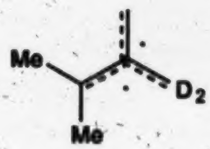
Scheme 21

intermediates can not be ruled out experimentally by a comparison with products formed by the thermolysis of *cis*-3,5-dimethyl-4-methylene-1-pyrazoline **125** since the Chesick diradicals **185** and **186** are likely to be formed in different proportions from pyrazolines **125** and **126**, which in turn would explain their differing product ratios (Table 11). Planar intermediates such as **190** have been ruled out[17] since **190** would be a common intermediate for **53** and **34** thermolysis (Scheme 22); however the same product ratios were not obtained. Current thinking[17,18], however, precludes this conclusion since products are likely to be generated from primary diazenyl radicals.



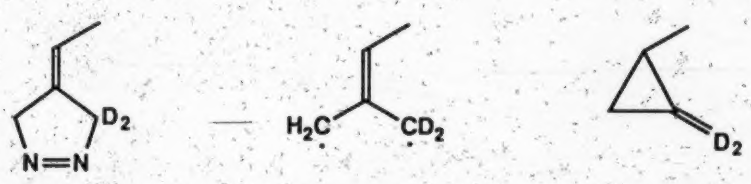
Scheme 22

Crawford *et al.* [5] suggested that the cleavage of the C_5-N bond of **29** (Scheme 15) would produce an unstable diradical intermediate **90** which would quickly form Chesick diradical **89**. If this diradical became planar as in **191**, products could still be rationalized, as previously described, by sigma bond formation between the isopropylidene and an adjacent methylene termini (i.e., Chesick diradical behavior). However, it is difficult to perceive that products would not also be formed by sigma bond formation between the two methylene termini. It is possible that the stability of the isopropylidene radical formed by rotation out of the plane might promote bond formation between the isopropylidene and the adjacent methylene termini.



191

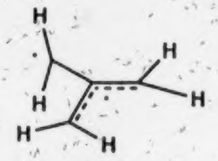
Dolbier and Burkholder[8] have suggested that the thermolysis products of Z-3-dideuterio-4-ethylidene-1-pyrazoline **19** can be rationalized in terms of a partly equilibrated set of orthogonal trimethylenemethane (TMM) intermediates and planar TMM such as **192** (Eq. 44). Unlike the fully delocalized planar TMM such as **190** and **191**, the planar **192** maintains a stereochemical uniqueness by the presence of a double bond and two allylic radicals. Although they point out that **192** does not need to be totally planar to rationalize their results, the planar TMM is required to explain the loss of optical activity obtained in our work during the thermolysis of optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126**.



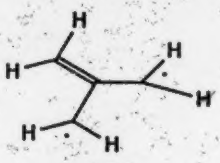
19 192 94

(Eq. 44)

Borden *et al.*[38] provide some theoretical support for intermediates similar to **192**. Using a variety of basis sets, they located the optimum singlet geometries for the parent TMM by varying methylene rotational angles. They also calculated transition state energies in the transformation of the singlet minima to the product methylenecyclopropane. A contour map[38] of their results is shown in Figure 11. Their results confirmed others[41,42] in that the orthogonal TMM **122** is the lowest energy TMM singlet. Located ~6 kcal above **122** was the lowest planar TMM **123** (similar to **192**) which could form the product MCP by either conrotatory or disrotatory movement. More importantly, as can be seen in Figure 11, the transition states connecting TMM **122** and **123** to the product MCP are of similar total



122
orthogonal singlet
C_{2v} ($^1B_1$)



123
planar singlet
C_{2v} ($^1A_1$)

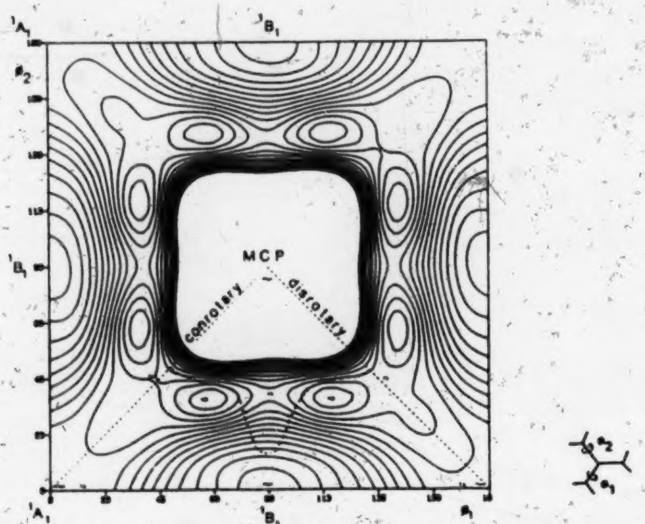
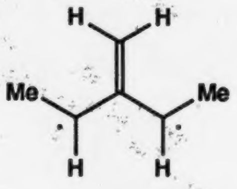
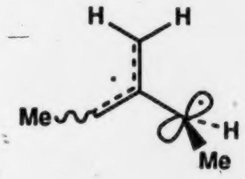


Figure 11. Contour map of the lowest singlet potential energy surface of the methylenecyclopropane rearrangement as a function of two rotational angles with all other geometrical parameters optimized. Increments are 0.001 hartree. Reprinted with permission from D.Feller, K.Tanaka, E.R.Davidson, and W. T. Borden. J. Am. Chem. Soc. 104, 967 (1982). Copyright 1982, American Chemical Society.

energy. They also estimated that the barrier between orthogonal TMM **122** and planar **123** was slightly lower than the transition state energy between **123** and the product MCP, thus the conversion between orthogonal TMM **122** and planar TMM **123** and product formation from either would be competitive processes. Also, since the energy surface around planar TMM **123** is fairly flat they suggest that partitioning of intermediate **123** could be influenced by molecular dynamics. The introduction of methyl groups to **123** to form **193** would lower the energy of the planar **123** due to the stabilizing nature of the methyl groups; however, steric effects could counteract this benefit to favour the orthogonal TMM **185** or **186**.

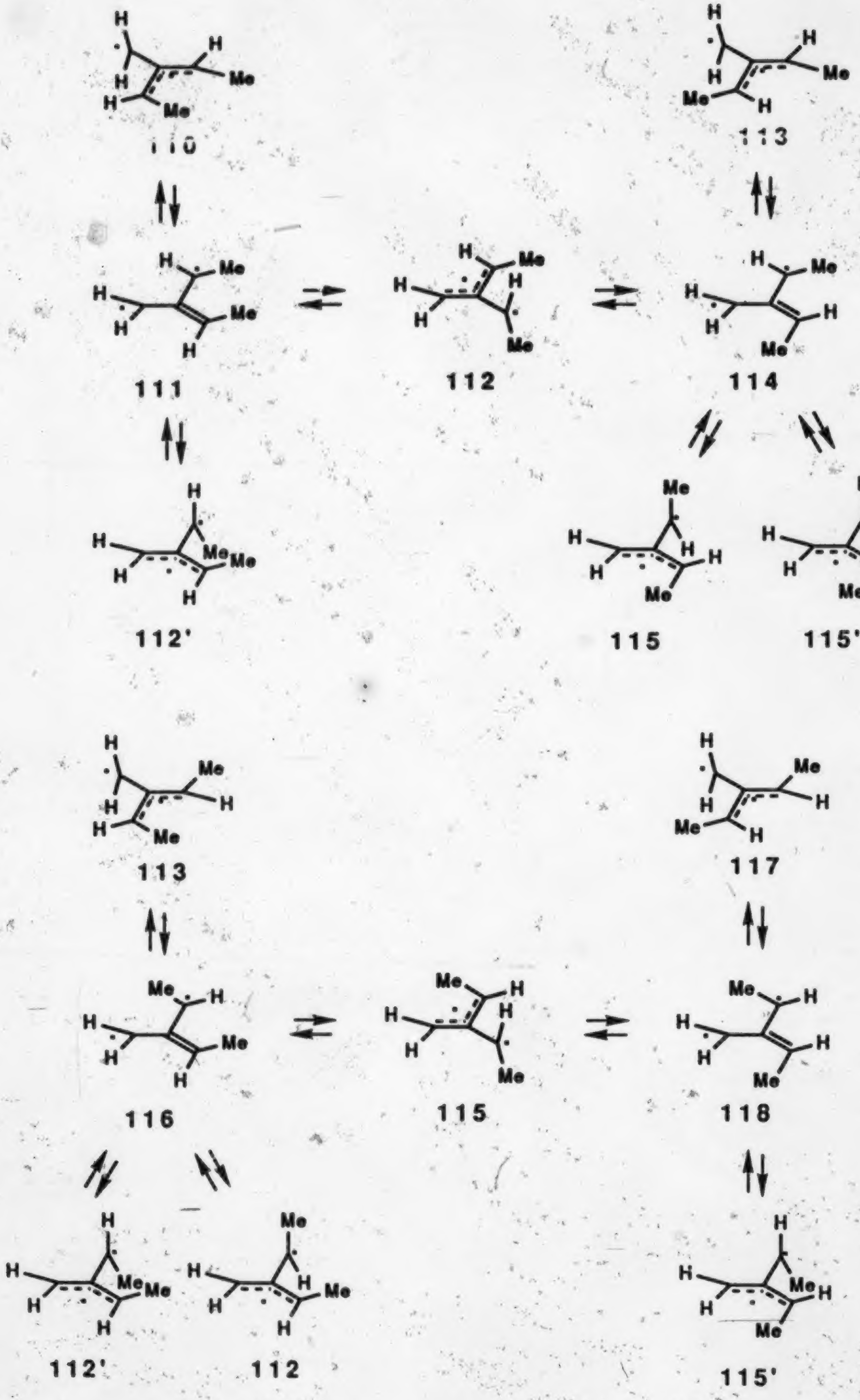


193



185 or **186**

In terms of the thermolysis of optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126**, the orthogonal Chesick diradicals **112** and **115** (scheme 12) would be formed by nitrogen loss from diazenyl radicals **82** and **90** respectively. The orthogonal diradicals **112** and **115** differ only by a 180° rotation of the allylic ethylidene group. The achiral planar TMM **111**, **114**, **116**, and **118** that would account for the absence of optical activity in the product alkylidenecyclopropane products could be obtained by a 90° rotation of the orthogonal ethylidene group of **112** and **115** in either direction. A 90° rotation of the allylic ethylidene radical terminus of

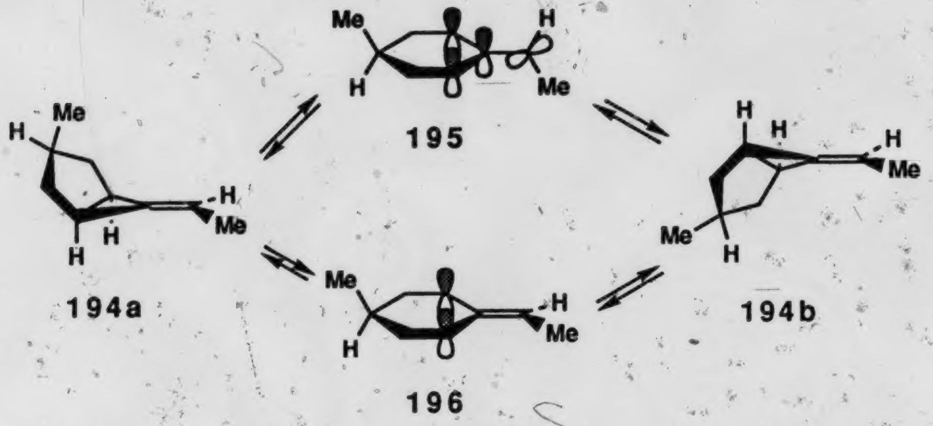


Scheme 12

111 would produce the enantiomeric pair **112** and **112'**, while a similar rotation of **114** would produce the enantiomeric pair **115** and **115'**. Analogously **116** and **118** would produce the enantiomeric pairs **112**, **112'** and **115**, **115'** respectively. Since optically active products can be generated from ring closure of the initially formed chiral orthogonal TMM **112** and **115**, the total loss of optical activity would require that formation of the planar TMM be more rapid than product formation from the orthogonal TMM.

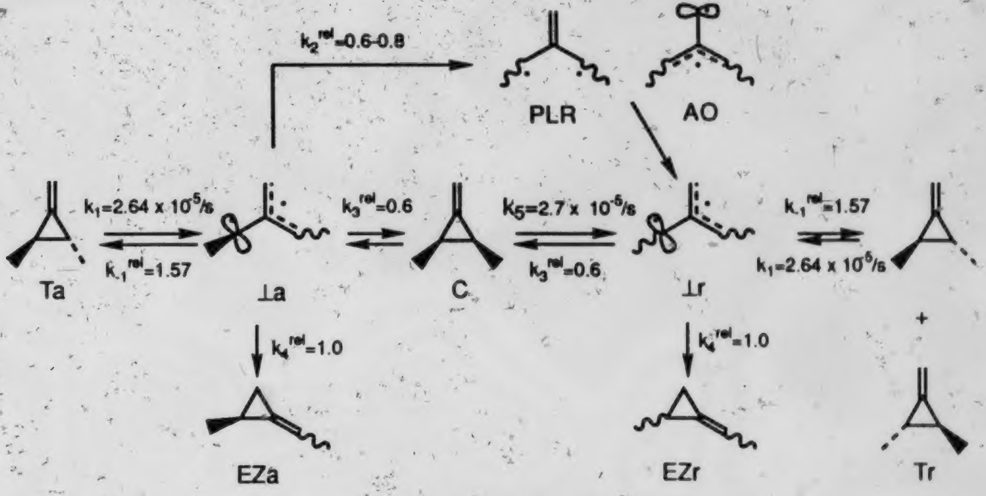
Differing amounts of orthogonal TMM **112** and **115** (and therefore differing amounts of the two sets of equilibria) generated by the thermolysis of *cis* **125** and *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126** could account for their differences in product ratios. It is essential that total equilibrium is not attained since the two sets of intermediates are not exclusive to each set. Total equilibrium would lead to identical product ratios from **125** and **126**. Molecular dynamics and steric effects could influence the relative amounts of **111** and **114** and the relative amounts **116** and **118** produced from orthogonal TMM **112** and **115** respectively.

A small amount of planar TMM may have been observed by Roth[66] and Gajewski[36] in similar experiments. Both found that the thermolysis of one chiral methyl-substituted diastereomer of 6-ethylidenebicyclo[3.1.0]-hexane **194a** produced ~8-10% of the other diastereomer **194b** with retention of stereochemistry in the exo ethylidene group. Represented in Scheme 23[66] , the conversion of diastereomers **194a** and **194b** could occur either via the lower energy othogonal TMM species **195** or the planar TMM **196**. Thus any loss of exo ethylidene stereochemistry would occur through the orthogonal TMM **195** (i.e., since rotation of the orthogonal group would result in both retention and inversion of the exo ethylidene) while retention of stereochemistry would occur via the planar TMM **196**. Since net retention of stereochemistry occured it was deemed that the formation of planar TMM was energetically possible.



Scheme 23

Gajewski and Chou[36] have studied the rates of isomerization and racemization of a thermolysed sample of optically active *trans*-2,3-dimethylmethylenecyclopropane **Ta** (Scheme 24). They proposed that initially an optically active orthogonal TMM **⊥a** was formed reversibly which would generate either optically active E and Z-2-methylethylidenecyclopropane **EZa** (essentially irreversibly) by inversion of stereochemistry at the orthogonal pivot point or generate the achiral *cis*-2,3-dimethyl–methylene–cyclopropane **C**. A racemic orthogonal TMM **⊥r** would be formed reversibly from achiral **C** and would generate essentially irreversibly E and Z-2-methylethylidenecyclopropane **EZr** and reversibly racemic **Tr**. Being unable to mathematically account for the total racemization of optically active *trans*-2,3-dimethylmethylenecyclopropane by ring opening of **C**, Gajewski proposed that the formation of an achiral planar TMM occured between 15-33% of all ring opening events of **T**. This conclusion is in agreement with Borden's calculations[38], i.e., the transition state energies linking the orthogonal and planar TMM with the product MCP are similar in energy.



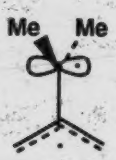
Scheme 24

Gajewski's results are particularly interesting since, although the two possible diastereomeric orthogonal TMM produced are identical (though not necessarily in the same ratio) to those that would be produced by the thermolysis of optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126** (Scheme 12), in contrast to our results some optical activity in the E and Z-2-methylethylidenecyclopropanes was obtained. It is still possible to bring the two results into concordance if molecular dynamics, possibly caused by the loss of nitrogen, prejudices the formation of a planar TMM in our study, i.e., the kinetic energy of the orthogonal group assists in overcoming the potential barrier to the planar TMM. It is also possible that our observed fully racemic product may be produced by a combination of

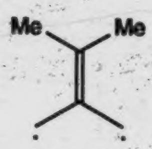
Chesick diradical formation from a partly rotamer equilibrating diazenyl radical species and the formation of planar TMM from these orthogonal Chesick diradicals.

In summary, although during thermolysis 4-alkylidene-1-pyrazolines appear to behave uniformly in terms of an initial rate determining one-bond homolysis to form diazenyl radicals, their product forming step(s) differ greatly. The mechanism used seems to be directly related to the stability of the alkyl radical that would be generated upon nitrogen loss from the appropriate diazenyl radical. A primary diazenyl radical has a large potential barrier to nitrogen loss; thus product formation directly from the diazenyl radical is favoured. In contrast, a tertiary diazenyl radical would quickly lose nitrogen to form a stable Chesick diradical from which products would be formed. The intermediate stability of a secondary alkyl radical appears to cause a diazenyl radical that is long lived enough to possibly allow equilibration of its rotamers; however, nitrogen is lost prior to product formation. If one assumes that total racemization does not occur by diazenyl radical rotation, then the orthogonal Chesick diradical must face a lower barrier to generate a planar TMM than to generate the product MCP.

If indeed tertiary diradicals do not form planar TMM, the difference in behavior of tertiary vs secondary diradicals (as would likely be generated in the thermolysis of **126**) may be explained in terms of methyl group stabilization in the orthogonal vs planar TMM. As can be seen by comparing **197** and **198** the radical stabilization in **197** by two methyl groups is totally lost in going to the planar TMM **198**, thus leading to a large energy barrier. A comparison of **199** and **200** reveals that both have one lone electron stabilized by a methyl group; however the allylic "half" electron stabilized in **199** is lost in the planar **200**. This minor difference suggests that a smaller energy barrier would be present in converting orthogonal **199** to planar **200**. Steric effects are also likely to influence the potential energy of the orthogonal and planar TMM - particularly the latter. This energy increase is likely on the average smaller in the planar **200**, particularly when the methyls are oriented away from each other as in the conformer **201**. Thus the energy separating **197** and **198** would be magnified relative to that separating **199** and **200**.



197



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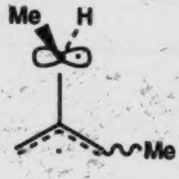

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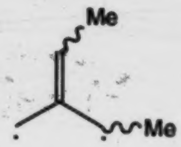

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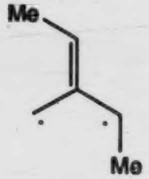
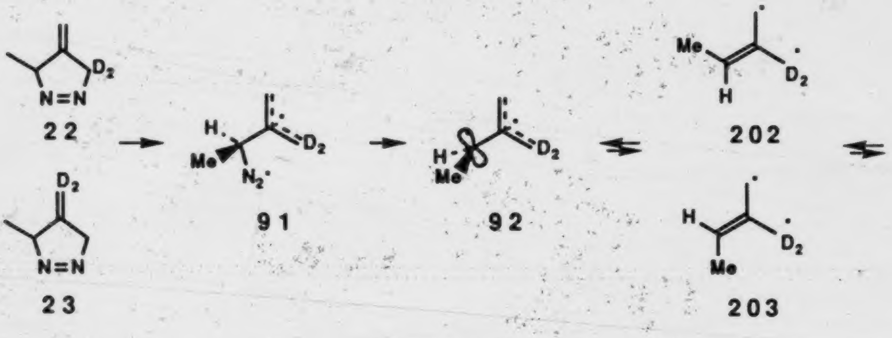


201

Unfortunately, the complex thermolysis product formation mechanism of 4-alkylidene-1-pyrazolines with secondary allylic endocyclic carbons, results in excessive difficulties in rationalizing product distributions both quantitatively and qualitatively (i.e., ethylidenecyclopropanes **99** and **108** - Scheme 10 and 11). As was pointed out in the introduction, KIE indicated that the thermolysis of dideuterio 3-methyl-4-methylene-1-pyrazolines **22** and **23** should cleave almost exclusively at the C_5-N bond[5] (Scheme 25). They should therefore produce identical intermediates, however product ratios from the two pyrazolines differ. This dilemma is likely not solved by the possible formation of the planar TMM **202** and **203** since again identical intermediates (and also their proportions) should be formed, particularly if free rotation of the diazenyl radical randomizes the location of the methyl group before nitrogen loss. Molecular dynamics created by nitrogen loss from unequilibrated rotamers generated from **22** and **23** might lead to a selectivity between planar **202** and **203**. Since this work does not substantiate product formation from the diazenyl radical **91**, ring closure from planar **202** and **203** or from orthogonal TMM's generated from **202** and **203** could form the 18-20% of ethylidenecyclopropanes observed experimentally. It is possible, however, that these results may be explained by products formed from the intermediates generated by the minor cleavage of the C_3-N bond, particularly since a deuterium KIE would lead to more C_3-N bond cleavage in **22**.



Scheme 25

EXPERIMENTAL

All boiling and melting points are reported uncorrected.

Preparative scale gas chromatographic separations and analytical analyses were achieved on a Varian Aerograph Series 1400 GC connected to a Hewlett Packard 3370A integrator and a Fisher Recordall Series 500 strip chart recorder. Unless otherwise indicated, the packed column used was a 6.1 meter x 3.2 millimeter stainless steel column filled with 15 % OV 101 on Chromosorb Paw.

Capillary gas chromatographic analyses were achieved on a Hewlett Packard 5840A GC using a 12 meter x 0.20 millimeter i.d. methyl silicone fused silica capillary column.

High performance liquid chromatographic (HPLC) separations were done on a Waters system consisting of: a Model 600A solvent delivery system, a Lambda-Max Model 480 LC spectrometer (UV detector), a M730 Data Module, and a rheodyne injector system.

Thermolyses were conducted in a well insulated oil bath controlled by a Melabs Model CTCIA proportional temperature controller and measured by a HP Model 2801A quartz thermometer calibrated by the National Bureau of Standards.

Proton and carbon nuclear magnetic resonance spectra were obtained on a Bruker WH-200, a Bruker AM-300, and a Bruker AM-400 high field cryospectrometers and a Bruker WP-80 spectrometer.

Exact masses were determined on a Krotus MS-50 mass spectrometer. Low ionization potential mass analyses were performed on a Krotus MS-12 mass spectrometer and a VG-70E GC mass spectrometer.

A Nicolet 7199 Fourier Transform Interferometer and a Hewlett Packard 5965A IRD GC-IR were used to obtain Fourier transform infrared spectra.

X-ray structures were determined on an Enraf-Nonius CAD4 automated diffractometer.

Ultra-violet and visible spectra were obtained on Hewlett Packard 8450A diode array spectrometer.

Optical rotations were determined on two Perkin-Elmer 241 polarimeters.

Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Alberta.

3-Methyl-2,4-pentanedione (136)

3-Methyl-2,4-pentanedione was prepared by one of the methods offered by Johnson, Markham, and Price[44]. Acetylacetone (186 g, 1.85 mole), methyl iodide (344 g, 2.42 mole), and anhydrous potassium carbonate (240 g, 1.74 mole) were placed in a 2-*l*. flask equipped with a mechanical stirrer. After refluxing gently for 8 h, the mixture was cooled and 350 ml of petroleum ether (bp 30-60°C) was added. Insoluble material was filtered off and washed with 700 ml of a 1:1 mixture of acetone-petroleum ether. The combined filtrate and washings were concentrated at 20 torr. Pure product (170 g, 1.49 mole, 80.5%) was obtained by distillation on a spinning band column. Bp 165-167°C / 708 torr (lit. bp 170-172°C / 760 torr[1]).

^{1}H NMR spectrum ($CDCl_3$, 200 MHz) δ: 61% as the dione, 3.69 (q, J=7.0Hz, 1H,), 2.20 (s, 6H), 1.34 (d, J=7.0Hz, 3H); 39% as the enol tautomer, 2.12 (s, 6H), 1.84 (s, 3H).

3-Methyl-3-phenylseleno-2,4-pentanedione (137)

The procedure used is an adaption of the methodology used by Renga and Reich[45]. 3-Methyl-2,4-pentanedione (44.9 g, 0.394 mole) was added to a 1000 ml 3-necked flask containing 550 ml of dry THF,and equipped with a mechanical stirrer and a 300 ml pressure equalizing dropping funnel. While under a gentle flow of nitrogen, 19.9 g of 66% sodium hydride in oil (0.548 mole, washed with 2 x 25 ml pentane) was added to the 0°C solution over a period of 20 minutes with the aid of 50 ml of dry pentane. This mixture was then warmed to room temperature for 1.5 h. After cooling the reaction mixture to 0°C , benzeneselenenyl chloride (80.0 g, 0.418 mole) in 100 ml of dry THF was quickly added. The solution was stirred at 0°C for 20 minutes, then poured into a rapidly stirred mixture of 800 ml of 1:1 ether-pentane, 200 ml of aqueous 7% sodium bicarbonate, and 200g of ice. The resulting immiscible layers were seperated and the aqueous layer extracted with 200 ml of 1:1 ether-pentane. The combined organic layers were washed with 100 ml brine, then dried by filtering through a cone of sodium sulfate. Evaporation of the solvent at 20 torr yielded a yellow oil from which white crystals of product (86.4 g, 0.321 mole, 81.5%) were obtained after crystallization and recrystallization from ether-pentane. Mp 41.5-42.5°C.

Anal. calcd. for $C_{12}H_{14}O_2Se$: C 53.54, H 5.24, O 11.89, Se 29.33. found : C 53.60, H 5.36, O 11.97, Se 29.07.

M/e (calcd. for $C_{12}H_{14}O_2Se$, 270.0145) 270.0154.

^1H NMR spectrum ($CDCl_3$, 80 MHz) δ: 7.4 (m, 5H), 2.33 (s, 6H), 1.54 (s, 3H).

5,5-Diacetyl-2-norbornene (138)

With the exception of the trapping of the oxidation-elimination product, the methodology used was that of Reich, Renga, and Reich[47]. 3-Methyl-3-phenylseleno-2,4-pentanedione (19.7 g, 73.2 mmole) was dissolved in 150 ml of dry dicloromethane. The 250 ml 3-necked flask containing the solution was equipped with a stoppered 25 ml pressure equalizing dropping funnel, a submerged gas inlet tube, a gas outlet tube hooked up to an oil bubbler, and a magnetic stirrer. Electrically generated ozone was passed through a gas coil, emersed in dry ice/acetone to remove water, and into the -78°C flask until the dichloromethane turned blue indicating excess ozone. The system was then purged of ozone and air with nitrogen gas for 15 minutes. To this -78°C solution was added dry potassium carbonate (20.0 g, 145 mmole) and freshly distilled cyclopentadiene. The heterogeneous solution was warmed to room temperature and rapidly stirred for 16 h. Water (150 ml) was added and the layers seperated. The aqueous layer was extracted with 75 ml of dichloromethane and the combined organic layers dried using 75 ml of brine and then sodium sulfate. After concentrating the solution at 20 torr, 100 ml of ether were added. The resulting precipitate was removed and the solution concentrated at 20 torr. Distillation of the concentrate gave 9.96 g (55.9 mmole, 74% yield) of pure product. Bp 61.5-63.5°C/0.06 torr.

Anal. calcd. for $C_{11}H_{14}O_2$: C 74.13, H 7.92, O 17.95. found: C 74.12, H 7.79, O 18.09.

M/e (calcd. for $C_{11}H_{14}O_2$, 178.0980) 178.0993.

I. r. (cm^{-1}): 1695, C=O stretch

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 6.13 (d of d, J=5.7Hz, 3.1Hz, 1H), 5.97 (d of d, J=5.7Hz, 2.9 Hz, 1H), 3.54 (b, 1H), 2.88 (b, 1H), 2.13 (d of d, J=12.3Hz, 2.8Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 1.92 (d of d, J=12.3Hz, 3.9Hz, 1H), 1.51 (m, 1H), 1.32 (bd, J=8.5Hz, 1H).

5,5-Bis-(1-hydroxyethyl)-2-norbornene (139)

Via lithium aluminum hydride reduction

Using a modification of the procedure used by Maier, Roth, and Schmidt[48], pulverized lithium aluminum hydride (31.5 g, 0.830 mole) and 500 ml absolute ether were heated to a reflux for 30 minutes in a 250 ml 3-necked flask while under a nitrogen atmosphere. After removing the heating mantle, 103 g (0.578 mole) of 5,5-diacetyl-2-norbornene in 100 ml ether was slowly added to the vigorously stirring solution (magnetic stir bar) via a 250 ml dropping funnel at a rate so as to maintain a gentle reflux. Refluxing was continued for another 16 h and then the reaction mixture was cooled to 0°C. Distilled water (32 ml), 15% sodium hydroxide (32 ml), and distilled water (96 ml) were added successively so as to destroy excess lithium aluminum hydride. This mixture was stirred for 2 h and then vacuum filtered. The removed solid was washed with hot ether (4 x 500 ml) combined and then concentrated at 20-torr to yield 125 g of crude product. Pure 5,5-bis-(1-hydroxyethyl)-2-norbornene (99.2g, 94.2%), as a mixture of isomers, was obtained by distillation. Bp 100-107°C / 0.1 torr.

Anal. calcd.for $C_{11}H_{18}O_2$: C 72.49, H 9.95, O 17.56. found : C 72.44, H 9.97, O 17.59.

M/e (calcd.for $C_{11}H_{18}O_2$, 182.1292) 182.1306.

I. r. (cm^{-1}): 2969, C-H stretch ; 3290 broad O-H stretch.

^1H NMR spectrum ($CDCl_3$, 300 MHz) δ: 0.30-2.10 (series of multiplets, 10H), 2.40-3.20 (series of broad singlets, 2H), 3.50-4.70 (series of multiplets, 4H), 6.00-6.35 (series of multiplets, 2H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: For 4 diastereomers require 44 lines, found 43 lines; 138.46, 138.25, 138.01, 137.41, 136.64, 136.44, 136.29, 134.52, 78.19, 77.86, 76.37, 76.08, 75.79, 75.42, 71.20, 70.87, 53.45, 53.09, 52.56, 52.36, 48.81, 48.34, 48.30, 48.24, 47.88, 47.73, 47.12, 44.50, 42.88, 42.47, 42.08, 41.95, 38.45, 33.75, 32.92, 30.31, 22.24, 21.73, 21.61, 21.52, 21.12, 19.27, 19.04.

5,5'-Spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (140)

Using a modified procedure of Evans, Parrish, and Long[67] a solution of 5,5-bis-(1-hydroxyethyl)-2-norbornene (99.2 g, 0.544 mole), 2,2-dimethoxypropane (460 ml, 3.74 mole), and 0.60 g of *p*-toluenesulfonic acid dissolved in 500 ml of dichloromethane was stirred in a 2-*l* round-bottom flask for 18 h. The reaction mixture was extracted with 500 ml of 5 % sodium bicarbonate, 250 ml of water, and 250 ml of brine. After drying over magnesium sulfate, the solution was concentrated at 20 torr. Distillation at 0.1 torr using a 6 inch Vigreux column gave 5,5'-spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (113 g, 0.508 mole, 93 %) as a mixture of isomers. Bp 65-83°C / 0.1 torr.

Anal. calcd. for $C_{14}H_{22}O_2$: C 75.63, H 9.97, O 14.39. Found : C 75.65, H 9.81, O 14.54.

M / e (calcd. for $C_{14}H_{22}O_2$, 222.1604) not found.

M / e (calcd. for $C_{13}H_{19}O_2$, 207.1370) 207.1385 – loss of $CH_3^{\bullet}$

I. r. (cm^{-1}): 2980 C-H stretch; 1377, 1367 H_3C-C-CH_3 bending; 3060, =C-H stretch.

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 6.0- 6.3 (series of multiplets, 2H), {[4.35 (q, J=6.5Hz), 4.14 (q, J=6.5Hz), 4.11 (q, J=6.5Hz), 3.91 (q, J=6.8Hz), 3.76 (q, J=6.5Hz), 3.75 (q, J=6.5Hz), 3.54 (q, J=6.8Hz), 3.51 (q, J=6.9Hz)], 2H}, {[2.98 (bs), 2.87 (bs), 2.79 (bs), 2.73 (bs), 2.34 (bs)], 2H}, 1.0-2.0 (series of multiplets, 16H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: For 4 diasteriomers expect 56 lines , found 56 lines: 140 07, 138.84, 138.65, 138.24, 136.83, 135.96, 135.54, 134.56, 99.28, 98.69, 98.30, 97.61, 77.81, 76.50, 75.95, 75.30, 73.17, 71.07, 69.86, 66.81, 51.67, 50.95, 50.70, 49.57, 49.02, 48.45, 48.37, 48.07, 47.66, 46.65, 46.29, 46.23, 42.71, 42.27, 41.83, 41.77, 40.79, 32.45, 31.91, 31.86, 31.18, 31.03, 30.91, 26.14, 25.63, 24.68, 23.28, 22.93, 22.15, 21.73, 20.86, 20.67, 19.76, 19.44, 18.50, 18.33.

2,2,4,6-Tetramethyl-5-methylene-1,3-Dioxane (141)

An adaption of the method used by Corey and Suggs[49] was utilized. The pyrolysis vessel consisted of a 50 cm quartz column (2.54 cm i.d.) packed with glass beads that was heated to 440-460°C by a heat tape wrapped around the column. Glass wool was used as an insulator between the tape and an outer pyrex jacket. The temperature was measured by an iron-constantan thermocouple and a potentiometer. A 250 ml pressure equalizing dropping funnel was attached to the top of the column. To the bottom was attached 3 traps hooked in series (cooled to -78°C). While under a pressure of 1.0 torr, 5,5'-spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (113 g, 0.508 mole) was added to the column at a rate of 1 drop/6 sec. After the addition the first trap was warmed to room temperature. Material that did not distill from this trap was re-thermolyzed. With the first trap at room temperature and the other two at -78°C distillation was continued for 3 h. The second and third trap contained 110 g of product and cyclopentadiene. 2,2,4,6-Tetramethyl-1,3-dioxane (68 g, 0.44 mole, 86 %) was isolated as a mixture of two isomers by a spinning band distillation. Bp 56-59°C/19.6 torr. Purity was greater than 98% by GC (6.1 m. OV101 column). *Trans* 52 %. *cis* 48 %.

Anal calcd. for $C_9H_{16}O_2$: C 69.19, H 10.32, O 20.48. Found: C 68.91, H 10.16, O 20.93.

M/e (calcd. for $C_9H_{16}O_2$, 156.1136) 156.1141.

Separation of the cis and trans isomers (>98 %) was achieved using a 230-400 mesh flash silica column impregnated with 17 % silver nitrate. Ethyl acetate-hexane 5 % was used as an eluent.

trans isomer:

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 4.78 (t, J=2.0Hz, 2H,), 4.46 (t of q, J=6.5Hz, 2.0Hz, 2H), 1.39 (s, 6H), 1.34 (d, J=6.5Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 155.49, 103.93, 100.17, 66.35, 25.12, 18.77.

cis isomer:

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 4.86 (t, J=2.0Hz, 2H), 4.44 (t of q, J=6.2Hz, 2.0Hz, 2H), 1.57 (s, 3H), 1.41 (s, 3H), 1.34 (d, J=6.2Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 148.58, 106.31, 98.55, 67.35, 29.93, 19.88, 18.24.

Diasteriomeric Product Studies in the Reduction of 5,5-Diacetyl-2-Norbornene (138)

Lithium Aluminum Hydride

See page 103.

1-Equivalent of Red-Al at 0°C

A modification of the procedure of Capka *et.al.* [68] was used for the reduction step. The reaction was done in a 50 ml 3-necked flask equipped with a 25 ml addition funnel while under a slow stream of nitrogen. To 5,5-diacetyl-2-norbornene (1.010 g, 5.67 mmole), dissolved in 5 ml of dry benzene at 0°C, was added dropwise 1.8 ml of 3.4M (6.12 mmole) Red-Al in toluene (with the aid of 5 ml benzene). Upon completion of the Red-Al addition, the flask was immediately warmed to room temperature and stirred for another 6 h. The reaction was quenched using the standard procedure by adding successively 1.6 ml water, 1.6 ml of 15% sodium hydroxide, and 4.8 ml water. After 30 minutes of stirring, magnesium sulfate was added to solidify the resulting gel. The solid was filtered off and washed with 50 ml of hot ether. Crude 5,5-bis-(1-hydroxyethyl)-2-norbornene (0.910 g) was obtained by concentrating the solution at 20 torr and then for 2 h at 0.1 torr.

The crude diol (0.901 g) was protected as an acetal by stirring for 40 h at room temperature in a 25 ml round bottom flask containing 10 ml of dry dichloromethane, 3.0 ml of 2,2-dimethoxypropane (24.7 mmole), and 5 mg of *p*-toluenesulfonic acid. The acid was then extracted with 10 ml of 5% sodium bicarbonate. After washing the dichloromethane layer with 10 ml of water and 10 ml of brine then drying over magnesium sulfate, the solution was concentrated at 20 torr. The product 5,5'-spiro-[2',2',4',6'-tetramethyl-

1',3'-dioxane]-2-norbornene (0.535 g, 2.41 mmole, 42.9 % from the dione) was obtained after a 230-400 mesh flash silica column using 6:1 hexane-ethyl acetate as the eluent. The product gave one spot on TLC and was >95 % pure by ^{13}C and ^{1}H NMR.

Using the procedure as described earlier for the synthesis of 2,2,4,6-tetramethyl-5-methylene-1,3-dioxane (p 105), 5,5'-spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (0.358 g, 1.73 mmole) was thermolysed at 450°C and 1.0 torr to yield 2,2,4,6-tetramethyl-5-methylene-1,3-dioxane as a mixture of two isomers in 63 % yield (0.171 g, 1.09 mmole). *Trans* 44 %, *cis* 56% by ^{1}H NMR and GC (6.1 m. OV101).

2-Equivalent of Red-Al at 0°C

Using essentially the same procedure as for 1-equivelent of Red-Al (see above) 3.6 ml of 3.4M Red-Al (11.6 mmole) in toluene was added to 5,5-diacetyl-2-norbornene (1.006 g, 5.64 mmole) in benzene at 0°C. The mixture was then stirred at room temperature for 3.5 h and worked up to yield 0.920 g of crude 5,5-bis-(1-hydroxyethyl)-2-norbornene.

5,5'-spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (0.672 g, 3.02 mmole, 54.6 % from the dione) was obtained by the reaction of the crude diol (0.902 g) in the presence of 3.0 ml (24 mmole) of 2,2-dimethoxypropane containing 5 mg of *p*-toluenesulfonic acid. After the flash silica column the product 5,5-bis-(1-hydroxyethyl)-2-norbornene gave one spot on TLC and was >95% pure by ^{13}C and ^{1}H NMR.

Thermolysis of the acetal (0.522 g, 2.34 mmole) at 450°C and 1.0 torr gave 2,2,4,6-tetramethyl-5-methylene-1,3-dioxane in 57 % yield (0.209 g, 1.34 mmole) as a mixture of two isomers. *Trans* 43 %, *cis* 57 % by ^{1}H NMR and GC (6.1 m OV101 column).

1-Equivalent of Red-Al at -78°C

The reduction step was a modification of the procedure used by Capka *et. al.* [68]. The same apparatus as that for previous Red-Al reductions was used with the exception of the reaction flask being cooled to -78°C using a cryogenic bath. Red-Al (3.4 ml of 3.5M in toluene, 11.9 mmole) dissolved in 10 ml of additional toluene was added dropwise to a -78°C solution of 5,5-diacetyl-2-norbornene (2.02 g, 11.4 mmole) in 20 ml of toluene. The mixture was stirred for 4 h at -78°C then stirred overnight for an additional 10 h. During this time the temperature rose to -35°C. The reaction was quenched at 0°C with successive additions of 0.5 ml of water, 0.5 ml of 15 % sodium hydroxide, and 1.5 of ml water. The solution was stirred for 1 hour creating a gel that was solidified by the addition of 3 g of magnesium sulfate. The solid was filtered and washed with 4 x 30 ml of hot THF. Crude 5,5-bis-(1-hydroxyethyl)-2-norbornene (2.094 g) was obtained after concentrating at 20 torr and then 2 h at 0.1 torr.

The crude diol (1.958 g) was stirred for 16 h at room temperature in the presence of 2,2-dimethoxypropane (7.0 ml, 57 mmole) and 10 mg of*p*-toluene-sulfonic acid dissolved in 25 ml of dry dichloromethane. The reaction mixture was then washed with 2.0 ml of 5 % sodium bicarbonate, 10 ml of water, and 10 ml of brine. The dichloromethane solution was dried over magnesium sulfate, filtered, and concentrated at 20 torr. Chromatography over 230-400 mesh silica using 10:1 hexane-ethyl acetate gave 5,5'-spiro-[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (2.080 g, 9.36 mmole, 75.9 % from the dione). The product gave 1 spot on TLC and was >95 % pure by ^{13}C and ^{1}H NMR.

Thermolysis of the acetal (2.057 g, 9.25 mmole) at 450°C and 1.0 torr using the usual apparatus and procedure (p 105) gave 2,2,4,6-tetramethyl-5-methylene-1,3-dioxane (0.816 g, 5.24 mmole, 57 %) as a mixture of two isomers. *Trans* 46 %, *cis* 54 % by GC (6.1 m. OV101 column).

2.8-Equivalent of Dibal-H at -78°C

The general procedure of Hayakawa and Noyori[69] was used for the reduction of the diketone. The 250 ml round-bottom flask cooled at dry ice / acetone temperatures was equipped with an oil bubbler and a magnetic stirrer. A slow argon stream was maintained throughout the reaction. To the rapidly stirring 5,5-diacetyl-2-norbornene (1.997 g, 11.2 mmole) in 75 ml of dry THF at -78°C was added 30 ml of Dibal in hexane (28.1 mmole) over a 30 minute period. The mixture was stirred for 7 h. Dibal was destroyed by successive additions of 1.2 ml water (at -78°C) and 1.2 ml of 15 % sodium bicarbonate (at -78°C). The flask was warmed to room temperature and another 3.6 ml of water added. Magnesium sulfate (5 g) was added to solidify the resulting gel. The mixture was filtered and the solid washed with 3 x 50 ml of hot THF. Removal of the solvent at 20 torr, then 2 h at 0.1 torr gave 2.213 g of crude 5,5-bis-(1-hydroxyethyl)-2-norbornene.

Protection of the diol as an acetal, followed by thermolysis was done as outlined previously. Crude diol (2.11 g) was stirred for 13 h in the presence of 2,2-dimethoxypropane (7.0 ml, 57 mmole) and 10 mg of *p*-toluenesulfonic acid dissolved in 25 ml of dry dichloromethane. The reaction mixture was washed with 25 ml of 5 % of sodium bicarbonate, 10 ml of water, and 15 ml of brine. The organic layer was dried over magnesium sulfate , filtered and concentrated at 20 torr. Chromatography over 230-400 mesh silica using 10:1 hexane-ethyl acetate gave 5,5'-spiro-

[2',2',4',6'-tetramethyl-1',3'-dioxane]-2-norbornene (1.814 g, 8.16 mmole, 71.6 % from the dione). The product gave 1 spot on TLC and was >95 % pure by ^{13}C and ^{1}H NMR.

Thermolysis of the acetal (1.478 g, 6.65 mmole) at 450°C and 1.0 torr using the usual apparatus and procedure (p 105) gave 2,2,4,6-tetramethyl-5-methylene-1,3-dioxane (0.818 g, 5.24 mmole, 57 %) as a mixture of two isomers. *Trans* 46 %, *cis* 54 % by ^{1}H NMR and GC (6.1 m. OV101 column).

meso-3-Methylene-2,4-pentanediol (**142a**)

Using a modification of the procedure of Salomaa and Kankaanperä[50] 2,2,4,6-tetramethyl-5-methylene1,3-dioxane (7.88 g, 50.4 mmole, >98% *meso*) was stirred for 4.5 h at room temperature in a solution of 5 ml of 3N HCl in 50 ml of 95 % ethanol. The acid was neutralized with 0.4 g of sodium bicarbonate. After filtering off the solid, the solution was concentrated at 20 torr, and the residue distilled to yield pure 3-methylene-2,4-pentanedione (5.22 g, 44.9 mmole, 89 %). Bp 72-74°C /0.1torr. The diol was of >98 % *meso* configuration by ^{1}H NMR.

Anal. calcd. for $C_6H_{12}O_2$: C 62.04, H 10.41, O 27.55. Found : C 61.83, H 10.39, C 27.78.

M/e (calcd. for $C_6H_{12}O_2$, 116.0824) none found.

M/e (calcd for $C_5H_9O_2$, 101.0590) 101.0603 – loss of $CH_3^{\cdot}$.

M/e -NH_3 chemical ionization (calcd for $C_6H_{12}O_2 \cdot NH_4^+$, 134) 134.

I. r. (cm^{-1}): 3340, O-H stretch ; 1650, C=C stretch ; 1087 C-O stretch.

Elemental analysis, mass spec., and I.r. are from a mixture of *meso* and *rac* diol.

^{1}H NMR spectrum (CDCl$_3$, 300 MHz) δ: 5.12 (s, 2H), 4.41 (q, J=6.5Hz, 2H), 3.03 (s, 2H), 1.37 (d, J=6.5Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 155.24, 109.24, 69.02, 22.56.

rac-3-Methylene-2,4-Pentanediol (142b)

Using a modification of the procedure of Salomaa and Kankaanperä[50] 2,2,4,6-tetramethyl-5-methylene-1,3-dioxane (5.06 g, 32.4 mmole) was stirred for 4 h at room temperature in a solution of 5 ml of 3N HCl in 50 ml of 95 % ethanol. The acid was neutralized with 0.4 g sodium bicarbonate. After filtering off the solid, the solution was concentrated at 20 torr, and the residue distilled to yield pure 3-methylene-2,4-pentanedione (3.01 g, 25.9 mmole, 80.2 %). Bp 53-54°C / 0.15 torr. Mp 40-42°C. The diol was of >98 % *rac* configuration by ^1H NMR.

^1H NMR spectrum ($CDCl_3$, 300 MHz) δ: 5.08 (s, 2H), 4.50 (q, J=6.4Hz, 2H), 3.06 (b, 2H), 1.36 (d, J=6.4Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 54.10, 110.44, 69.05, 22.17.

meso-3-Methylene-2,4-dichloropentane (143a)

Using triphenylphosphine / carbon tetrachloride (65-70°C)

An adaption of the methodology of Hooz[70] was used. The reaction vessel, a 250 ml 3-necked flask equipped with a reflux condenser and thermometer, was kept under an argon atmosphere and heated by an oil bath. *Meso*-3- Methylene-2,4-pentanediol (6.60 g, 56.8 mmole, >98 % *meso*) was dissolved in 50 ml of CCl_4 and 15 ml of THF. Triphenylphosphine (35.8 g, 136 mmole) was added over a 10 minute period. The reaction was maintained between 65-70°C for 100 minutes, during which time a large quantity of white solid formed. After cooling to room temperature the stirring reaction mixture was placed at 50 torr for 1 h to remove solvent. The product *meso* -3-methylene-2,4-dichloropentane and isomers (6.09 g, 39.8 mmole, 70.0 %) were obtained by trapping at 0.8 torr and -78°C the remaining volatile portion of reaction mixture. ^{1}H NMR and GC (6.1 m. OV101 column) indicated product (including isomers) at >90 % purity. By ^{1}H NMR *meso* -3-methylene-2,4-dichloropentane 69 %, *rac*-3-methylene-2,4-dichloropentane 10 %, E-2-ethylidene-1,3-dichlorobutane 21 %.

M / e (calcd. for $C_6H_{10}{}^{35}Cl_2$, 152.0157) 152.0161.

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 5.42 (s, 2H), 4.90 (q, J=6.5Hz, 2H), 1.73 (d, J=6.5Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 152.62, 115.19, 56.42, 25.00.

Using hexamethylphosphorus triamide and trichlorofluoromethane

Using an adaption of the method suggested by Hooz[71] *meso* -3-methylene-2,4-pentanediol (2.78 g, 23.9 mmole) was dissolved in a 250 ml 3-necked flask containing 130 ml of dry trichlorofluoromethane and 50 ml of dry ether, and equipped with a reflux condenser, . With the flask under an argon atmosphere and at 0°C hexamethylphosphorus triamide (8.6 g, 52.7) dissolved in 25 ml ether was added via a dropping funnel over a 15 minute period. Stirring for 15 minutes more at 0°C resulted in a white precipitate. The reaction was warmed to room temperature for 2 h and then stored at -30°C overnight. Following removal of this solid by filtration and washing it with 50 ml of ether, the majority of the solvent was removed at 130 torr using a spinning band column. The distillation residue was flash distilled at <0.1

torr using a series of progressively colder U-tube traps (-25°C, -60°C, -80°C, -195°C). Trap 1 (-25°C) contained product (1.305 g, 8.64 mmole, 36.1 %) as a mixture of isomers. Purity >90 % by ^{1}H NMR. *meso*-3-Methylene-2,4-dichloropentane 80 %, *rac*-3-methylene-2,4-dichloropentane 18 %, E-2-ethylidene-1,3-dichlorobutane 2 % by ^{1}H NMR.

cis-5,7-Dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]-triazolidine-1,3-dione **(144a)**

From *meso*-3-Methylene-2,4-dichloropentane **(143a)**

An adaption of the method of Rubottom and Chabala[53] was used. Under an argon atmosphere, sodium hydride (0.346 g of 60 % in oil, 8.64 mmole) was added slowly to a 0°C 50 ml 3-necked flask containing 4-phenylurazole (1.68 g, 9.49 mmole) dissolved in 30 ml of dry HMPA and 30 ml of dry THF. The flask was warmed to room temperature and stirred for 30 minutes untill no hydrogen gas was evolved. To this solution was added *meso*-3-methylene-2,4-dichloropentane (1.305 g, > 90 % pure, max. of 8.64 mmole) in 20 ml dry of THF from the above reaction. After stirring for 24 h, the reaction mixture was cooled to 0°C and sodium hydride (0.346 g of 60 % in oil, 8.64 mmole) was added. Stirring was continued for 70 h at room temperature after which water (50 ml) was slowly added to quench the reaction. The water was extracted with 6 x 50 ml of dichloromethane. After drying the combined extracts over sodium sulfate, the solution was concentrated at 20 torr. Purification on a 230-400 mesh flash silica column using 2:1 hexane-ethyl acetate as an eluent gave a mixture of triazolinediones (1.20 g, 4.67 mmole, min. 55 %). *cis*-5,7-Dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione

63 %. *trans*-5,7-Dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*]-[1,2,4]triazolidine-1,3-dione 12 %. E-5-Methyl-6-ethylidene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 25 %.by ^{1}H NMR.

Directly from *meso*-3-methylene-2,4-pentanediol (142a) *in situ*

In a one pot reaction, *meso*-3-methylene-2,4-pentanediol was converted to the dichloride using an adaption of the method suggested by Hooz[71] and then to the *cis* -triazolinedione using an adaption of the process used by Rubottom and Chabala[53]. *Meso* -3-methylene-2,4-pentanediol (300 mg, 2.58 mmole >98 % *meso*) was dissolved in 20 ml dry trichlorofluoromethane and 10 ml absolute ether contained in a 100 ml 3-necked flask equipped with a reflux condenser and under argon, containing. After cooling the solution to -78°C hexamethylphosphorus triamide (1.09 g, 6.68 mmole) was added to the mixture. The flask was warmed to room temperature and stirred for 3 h, then stored at -35°C for 12 h. Freon and ether where removed from the dichloride by a flash distillation at 100 torr without warming. In a separate flask (under argon) sodium hydride (103 mg of 60 % in oil, 2.58 mmole) was added to a 0°C solution of 4-phenylurazole (0.458 g, 2.59 mmole) in 10 ml of dry THF and 5 ml of dry HMPA. This solution was stirred for 30 minutes at room temperature then added to the room temperature dichloride solution with a double ended needle. After 12 h of stirring the reaction mixture was cooled to 0°C and sodium hydride (103 mg of 60 %in oil, 2.58 mmole) added. Stirring was continued for 48 h at room temperature. Water (25 ml) was carefully added to the 0°C mixture and the product extracted with 5 x 25 ml of dichloromethane. The solution was concentrated at 20 torr then run on a 230-400 mesh flash silica column using 2:1 hexane/ethyl acetate as an eluent. Product triazolinedione (114 mg, 0.443 mmole 17.5 %) was obtained as a mixture of isomers : *cis* -5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 54 %, *trans* -5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 14 %, E-5-methyl-6-ethylidene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]-triazolidine-1,3-dione 32 %.by ^{1}H NMR.

rac -3-Methylene-2,4-Dichloropentane (143b)

Using Tributylphosphine and Carbon Tetrachloride

The procedure used was a modification of the method used by Hooz[70,71]. To *rac*-3- Methylene-2,4-pentanediol (0.201 g, 1.72 mmole, >98 % trans) dissolved in 3 ml of CCl_4 and 1 ml of THF (0°C) was added tributylphosphine (5.4 g, 20.6 mmole) over a 10 minute period. The exothermic reaction was maintained at 0°C for 0.5 h then warmed to room temperature. Stirring was continued for 40 h. Products and solvent were flash distilled at 0.2 torr and trapped at -78°C. Evaporation of the solvent at 50 torr gave *rac*-3-methylene-2,4-dichloropentane and isomers (0.11 g, 0.72 mmole, 42 %) ^{1}H NMR and GC (6.1 m. OV101 column) indicated product (including isomers) to be >90 % pure. By ^{1}H NMR *rac*-3-methylene-2,4-dichloropentane 61 %, *meso*-3-methylene-2,4-dichloropentane 14-%, E-2-ethylidene-1,3-dichlorobutane 25 %.

M/e (calcd. for $C_6H_{10}{}^{35}Cl_2$, 152.0157) 152.0163.

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 5.40 (s, 2H), 4.82 (q, J=6.5Hz, 2H), 1.72-(d, J=6.5Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 150.84, 113.15, 55.94, 23.08.

Using triphenylphosphine / carbon tetrachloride (40°C)

An adaption of the methodology of Hooz[70] was used. The reaction vessel, a 50 ml 3-necked flask equipped with a reflux condenser and thermometer, was kept under an argon atmosphere and heated by an oil bath. *rac*-3-Methylene-2,4-pentanediol (1.0 g, 8.60 mmole, >98 % *rac*) was dissolved in 10 ml CCl_4 and 3 ml THF. Triphenylphosphine (5.4 g, 20.6 mmole) was added over a 10 minute period. The exothermic reaction was maintained at 40°C for 7 h, during which time a large quantity of white solid formed. After cooling to room temperature the stirring reaction mixture was placed at 0.1 torr. Products and solvent were trapped at -78°C. Evaporation of the solvent at 50 torr gave *rac*-3-methylene-2,4-dichloropentane and isomers (0.82 g, 5.3 mmole, 62 %). ^{1}H NMR and GC (6.1 m. OV101 column) indicated the product (including isomers) to be >90 % pure. By ^{1}H NMR *rac*-3-methylene-2,4-dichloropentane 89 %, E-2-ethylidene-1,3-dichlorobutane 11%.

Using triphenylphosphine / carbon tetrachloride (60°C)

Using essentially the same procedure as above, *rac*-3-methylene-2,4-pentanediol (1.91 g, 16.42 mmole, >98 % *rac*) was dissolved in 20 ml CCl_4 and 6 ml THF. Triphenylphosphine (9.47 g, 36.12 mmole) was added over a 10 minute period. The exothermic reaction was maintained at 60°C for 3.5 h, during which time a large quantity of white solid formed. After cooling to room temperature the stirring reaction mixture was placed at 0.1 torr. Products and solvent were trapped at -78°C. Evaporation of the solvent at 50 torr gave *rac*-3-methylene-2,4-dichloropentane and isomers (1.38 g, 9.02 mmole, 52 %) ^{1}H NMR and GC (6.1 m. OV101 column) indicated product (including isomers) at >90 % purity. By ^{1}H NMR *rac*-3-

methylene-2,4-dichloropentane 79 %, *meso*-3-methylene-2,4-dichloropentane 12-%, E-2-ethylidene-1,3-dichlorobutane 9 %.

Using triphenylphosphine / carbon tetrachloride (25°C)

Using essentially the same procedure as above, *rac*-3- methylene-2,4-pentanediol (1.0 g, 8.60 mmole, >98 % *rac*) was dissolved in 10 ml CCl_4 and 3 ml THF. Triphenylphosphine (5.4 g, 20.6 mmole) was added over a 10 minute period. The exothermic reaction was maintained at room temperature for 24 h, during which time a large quantity of white solid formed. Products and solvent were flash distilled at 0.1 torr and trapped at -78°C. Evaporation of the solvent at 50 torr gave *rac*-3-methylene-2,4-dichloropentane and isomers (0.76 g, 5.0 mmole, 58 %) ^{1}H NMR and GC (6.1 m. OV101 column) indicated product (including isomers) at >90 % purity. By ^{1}HMR *rac*-3-methylene-2,4-dichloropentane 85 %, *meso*-3-methylene-2,4-dichloropentane 6-%, E-2-ethylidene-1,3-dichlorobutane 9 %.

trans -5,7-Dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]-triazolidine-1,3-dione (144b)

From *rac*-3-methylene-2,4-dichloropentane (143b)

An adaption of the method of Rubottom and Chabala[53] was used. Under an argon atmosphere, sodium hydride (26.1 mg of 60 % in oil, 0.653 mmole) was added slowly to a 0°C 50 ml 3-necked flask containing 4-phenylurazole (127 mg, 0.719 mmole) dissolved in 6 ml of dry HMPA and 2 ml dry of THF. The flask was warmed to room temperature and stirred for 30 minutes till no hydrogen gas was evolved. To this solution was added *rac*-3-methylene-2,4-dichloropentane (100 mg, > 90 % pure, max. of 0.653

mmole) in 2 ml dry THF from the above reaction. After stirring for 24 h, the reaction mixture was cooled to 0°C and sodium hydride (26.1 mg of 60 % in oil, 0.653 mmole) was added. Stirring was continued for 70 h at room temperature upon which water (20 ml) was slowly added to quench the reaction. The water was extracted with 6 x 20 ml of dichloromethane. After the combined extracts were dryed over sodium sulfate, the solution was concentrated at 20 torr. Purification on a 230-400 mesh flash silica column using 2:1 hexane-ethyl acetate as an eluent gave a mixture of triazolinediones (84.1 mg, 0.327 mmole, min. 50 %) : *trans* -5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 62%, *cis*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]-triazolidine-1,3-dione 8 %, E-5-methyl-6-ethylidene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 31 %.by ^{1}H NMR.

Directly from *rac*-3-methylene-2,4-pentanediol (142b) *in situ*

In a one pot procedure *trans* -3-methylene-2,4-pentanediol was converted to the dichloride using an adaption of the methodology of Hooz[70,71] and then to the *trans*-triazolinedione using an adaption of the process used by Rubottom and Chabala[53]. *rac*-3-Methylene-2,4-pentanediol (500 mg, 4.30 mmole >98 % *rac*) was dissolved in 100 ml 3-necked flask, equipped with a reflux condenser and under argon, containing 10 ml of dry trichlorofluoromethane and 10 ml of absolute ether. Hexamethylphosphorus triamide (1.55 g, 9.47 mmole) in 10 ml ether was added to the solution.at room temperature and then stirred for 2 h. The solvent and products were removed from the non-volatile material by flash distilling at 0.1 torr. Freon and ether where removed from the dichloride by flash distillation at 100 torr while the solution was being cooled by the heat of evaporation. In a separate flask (under argon) sodium hydride (160 mg of 60 % in oil, 4.00 mmole) was added to a 0°C solution of 4-phenylurazole (0.710 g, 4.00 mmole) in 10 ml of dry THF and 10 ml of dry HMPA. This solution was stirred for 30 minutes then added via a double ended needle to the room temperature dichloride solution. After 24 h of stirring the reaction mixture was cooled to 0°C and sodium hydride (160 mg of 60% in oil, 4.00 mmole) added. Stirring was continued for 48 h at room temperature. Water (100 ml) was carefully added to the 0°C mixture and the product extracted with 6 x 25 ml of dichloromethane. The solution was concentrated at 20 torr then run on a 230-400 mesh flash silica column using 2:1 hexane-ethyl acetate as an eluent. Product triazolinedione (532 mg, 2.07 mmole, 48 %) was obtained as a mixture of isomers : *trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 70 %, *cis*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione 8%, E-5-methyl-6-ethylidene-2-phenyl[1,2]diazolidino[1,2-a][1,2,4]triazolidine-1,3dione 22% by ^{1}H NMR.

Separation of triazolinedione isomers

The diasteriomers *trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione, *cis*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione, and E-5-methyl-6-ethylidenepyrazolidino[*d*]-2-phenyl-[2,4,8]triazolidine-3,5-dione were seperated on a 10 μ 25 cm x 21.1 mm i.d.chiral dinitrophenylglycine HPLC column (supplied by Regis Chemical Company, IL, USA). A 35 % isopropanol/hexane solution was used as an eluent. Under these conditions the elution order was *cis*, *trans*, then E-5-methyl-6-ethylidenepyrazolidino[*d*]-2-phenyl-[2,4,8]triazolidine-3,5-dione. Large overlap of peaks occurred on one pass through the column; therefore, recycling of the material and cutting of leading and trailing peaks was required.

cis -5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]-triazolidine-1,3-dione :

Mp. 146-146.5°C

Anal. calcd. for $C_{14}H_{15}N_3O_2$: C 65.36, H 5.88, N 16.33, O 12.44. found: C 65.25, H 5.92, N 16.17, O 12.66.

M/e (calcd. for $C_{14}H_{15}N_3O_2$, 257.1150) 257.1160.

I. r. (cm^{-1}): 1697.

^1H NMR spectrum ($CDCl_3$, 400 MHz) δ : 7.52 (m, 2H), 7.45 (m, 2H), 7.35 (m, 1H), 5.23 (t, J=2.4Hz, 2H), 4.60 (t of d, J=6.5Hz, 2.4Hz, 2H), 1.63 (d, 6.5Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 152.59, 152.37, 131.84, 129.11, 128.01, 125.50, 109.31, 56.32, 20.43.

trans-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*]-[1,2,4]triazolidine-1,3-dione :

Anal. calcd. for $C_{14}H_{15}N_3O_2$: C 65.36, H 5.88, N 16.33, O 12.44. Found : C 65.48, H 5.72, N 16.43, O 12.37.

M/e (calcd. for $C_{14}H_{15}N_3O_2$, 257.1150) 257.1164.

I. r. (cm^{-1}): 1697.

^1H NMR spectrum ($CDCl_3$, 400 MHz) δ: 7.52 (m, 2H), 7.45 (m, 2H), 7.35 (m, 1H), 5.24 (t, J=2.2Hz, 2H), 4.70 (t of d, J=2.2Hz, 6.8Hz, 2H), 1.61 (d, J=6.8Hz, 6H)

^{13}C NMR spectrum ($CDCl_3$, 75.5 MHz) δ: 152.51, 150.19, 131.88, 129.04, 127.90, 125.55, 109.20, 55.38, 18.98.

Separation of *trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]-diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione into its two enantiomers was accomplished using the chiral diphenylglycine HPLC column under the same conditions as reported in the preceding diasteriomeric separation.

cis -4-Methylene-3,5-dimethylpyrazolidine hydrochloride (145a)

The procedure used was an adaption of that used by Crawford and Tokunaga[29]. A typical reaction was as follows. To a 50 ml flask equipped with a reflux condenser and magnetic stirrer and under a slow stream of argon, containing 5 ml of *n* -propanol was added *cis*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione (200 mg, 0.777 mmole, > 98 % *cis*), EDTA (10 mg), and tetrabutylammonium iodide (10 mg). After refluxing this mixture for 15 minutes, potassium hydroxide (1.6 g) dissolved in 5 ml water was added. Refluxing was continued for 20 h. The cooled reaction mixture was transferred under argon to an argon flushed continuous extractor. After extracting for 3 h with ether, the ether was cooled to 0°C and excess hydrochloric acid (2.5 ml, 1 M, 2.5 mmole) was slowly added while stirring rapidly. The ether was removed at 20 torr and then at 0.1 torr for 24 h over phosphorus pentoxide to give a mixture of *cis*-4-methylene-3,5-dimethylpyrazolidine hydrochloride (>98 % *cis*) and aniline hydrochloride (224 mg, 45 mole % pyrazoline hydrochloride by ^{1}H NMR). The maximum possible yield is 216 mg ; therefore the sample may contain some potassium chloride.

^{1}H NMR spectrum ($CDCl_3$, 400 MHz) δ: 5.19 (t, J=2.3Hz, 2H), 4.14 (t of q, J=2.3Hz, 6.8Hz, 2H), 1.40 (d, J=6.8Hz, 6H).

^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz) δ: 153.20, 108.15, 59.78, 17.70.

trans -4-Methylene-3,5-dimethylpyrazolidine hydrochloride (145b)

The procedure used is an adaption of that used by Crawford and Tokunaga[29]. A typical reaction was as follows. To a 50 ml flask equipped with a reflux condenser and magnetic stirrer and under a slow stream of argon, containing 5 ml of *n*-propanol was added *trans*-5,7-dimethyl-6-methylene-2-phenyl[1,2]diazolidino[1,2-*a*][1,2,4]triazolidine-1,3-dione (130 mg, 0.505 mmole, > 98 % *trans*), EDTA (10 mg), and tetrabutylammonium iodide (10 mg). After refluxing this mixture for 15 minutes, potassium hydroxide (1.6 g) dissolved in 5 ml of water was added. Refluxing was continued for 20 h. The cooled reaction mixture was transferred under argon to an argon flushed continuous extractor. After extracting for 3 h with ether, the ether was cooled to 0°C and excess hydrochloric acid (2 ml conc. HCl) was slowly added while stirring rapidly. The ether was removed at 20 torr and then at 0.1 torr for 24 h over phosphorus pentoxide to give a mixture of *trans*-4-methylene-3,5-dimethylpyrazolidine hydrochloride (>98 % *trans*) and aniline hydrochloride (167 mg, 45 % pyrazolidine hydrochloride by ^{1}H NMR). The maximum possible yield is 141 mg ; therefore the sample may have contained some potassium chloride.

^{1}H NMR spectrum ($CDCl_3$, 400 MHz) δ: 5.20 (t, J=2.4Hz, 2H), 4.10 (t of q, J=6.6Hz, 2.4Hz, 2H)

^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz) δ: 152.89, 107.91, 60.02, 17.01.

cis -4-Methylene-3,5-dimethylpyrazoline (125)

An adaption of procedure of Crawford and Tokunaga[29] was used. In a typical reaction a mixture of *cis*-4-methylene-3,5-dimethylpyrazolidine hydrochloride (>98 % *cis*) and aniline hydrochloride (24 mg, 45 mole % pyrazolidine hydrochloride) was added to well stirred solution of red mercuric oxide (300 mg), sodium sulphate (300 mg), and anhydrous potassium carbonate (300 mg) in 15 ml of trichlorofluoromethane at 5°C. The reaction mixture was stirred for 36 h at 5°C, then filtered and the solid washed with 3 x 5 ml of trichlorofluoromethane. Aniline was removed by washing (at 5°C) with 5 x 2 ml of 0.1 M hydrochloric acid, 2 x 2 ml 5% sodium bicarbonate, 2 ml of water, and 2 ml of brine. After drying over magnesium sulfate, the solvent was removed by flash distillation using a series of cold traps (-25°C, -60°C, -80°C, -195°C) to selectively trap the product *cis* -4-methylene-3,5-dimethylpyrazoline (4.1 mg, 0.037 mmole, 53 %, >98 % *cis*). The product contained <5 % of trichlorofluoromethane.

^{1}H NMR spectrum (benzene d_6, 400 MHz) δ: 4.61 (t, J=2.6Hz, 2H), 4.35 (t of q, J=7.2Hz, 2.6Hz, 2H), 1.25 (d, J=7.2Hz, 6H)

M/e (calcd. for $C_6H_{10}N_2$, 110.0841) 110.0843.

trans -4-Methylene-3,5-dimethylpyrazoline (126)

A modification of the methodology of Barton, Lester, and Ley[54] was used. The following was a typical reaction. DABCO was added to a mixture of *trans* -4-methylene-3,5-dimethylpyrazolidine hydrochloride (180 mg), and aniline hydrochloride dissolved in 10 ml of dichloromethane. The mixture was stirred under argon for 10 minutes. Benzeneseleninic anhydride was added and the mixture stirred for 7 minutes. The product was flash distilled at 0.1 torr into a dry ice / acetone trap. Removal of DABCO was achieved by washing the dichloromethane with 4 x 2 ml of hydrochloric acid, 2 x 2 ml of sodium bicarbonate, 1 ml of water, and 1ml of brine. After drying over magnesium sulfate, the solvent was removed by flash distillation using a series of cold traps (-25°C, -60°C, -80°C, -195°C) to selectively trap the product *cis* -4-methylene-3,5-dimethylpyrazoline (4.1 mg, 0.037 mmole, 53 %, >98 % *cis*). The product contained <5 % trichlorofluoromethane.

^{1}H NMR spectrum ($CDCl_3$, 400 MHz) δ: 4.99 (t, J=2.4Hz, 2H), 4.91 (t of q, J=7.4Hz, 2.4Hz, 2H), 1.39 (d, J=7.4Hz, 6H)

M/e (calcd. for $C_6H_{10}N_2$, 110.0841) 110.0839.

Thermolysis of 3,5-dimethyl-4-methylenepyrazolines (125,126)

Diasteriomeric purity of the 3,5-dimethyl-4-methylenepyrazolines (dissolved in heptane) were determined with baseline resolution on a 12 m x 0.20 mm i.d. methyl silicone fused silica capillary column: Column, 35°C. Injector, 130°C. FID, 350°C. Split ratio, ~50:1. Sample size, 1 µl. The helium carrier flow rate was maintained so that methane travelled at a linear velocity of 20 cm/minute. Retention times were (minutes): *trans*-3,5-dimethyl-4-methylenepyrazoline **126** – 3.02, *cis*-3,5-dimethyl-4-methylenepyrazoline **125** – 3.14, E-3-methyl-4-ethylidenepyrazoline **99** - 4.14.(synthesized by the procedure of Crawford *et. al.*[65]). Low resolution GC-MS indicated all 3 peaks had a molecular weight of 110.

Thermolysis of *cis*-3,5-dimethyl-4-methylenepyrazoline **125** and racemic or optically active *trans*-3,5-dimethyl-4-methylenepyrazoline **126** produced 4 alkylidene cyclopropanes: *trans*-2,3-dimethylmethylenecyclopropane **131**, *cis*-2,3-dimethylmethylenecyclopropane **132**, E-2-methylethylidenecyclopropane **133**, and Z-2-methylethylidenecyclopropane **134**.

Thermolysis of the 3,5-dimethyl-4-methylenepyrazolines was conducted in breakseals of approximately 16 ml. Initial pressures at the reaction temperature of 170.0 ± 0.1°C were maintained at approximately

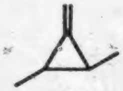
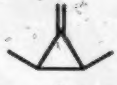
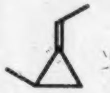
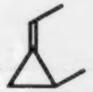
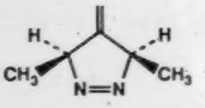
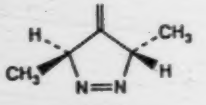
0.8-1.0 atmosphere. For the diasteriomeric product studies approximately 4 mg of sample were diluted with 250 µl of HPLC grade heptane (containing ~ 1 mg of deuterated benzene as an internal standard). This solution was divided into 5 samples that were vapor transferred into breakseals and then simultaneously thermolysed for a selected time period. After thermolysis the samples were quickly cooled in an ice-water bath and then vapor transferred into traps.

The diasteriomeric product study samples were directly analyzed with baseline resolution on the above column with the oven at -20°C.. All other conditions were identical. Retention times were (minutes): *trans*-2,3-dimethylmethylenecyclopropane **131** – (3.00), *cis*-2,3-dimethylmethylenecyclopropane **132** – (4.37), Z-2-methylethylidenecyclopropane **134** – (5.01), and E-2-methylethylidenecyclopropane **133** – (5.19). The identity of the alkylidenecyclopropanes was established by comparing retention times with authentic samples, by simultaneously injecting reaction and authentic samples, and by comparing the ^{1}H NMR analysis of a separate sample against the literature[72].

Samples for the thermolysis of chiral *trans*-3,5-dimethyl-4 methylenepyrazoline **126** were similarly handled except that approximately 45 mg of non-diluted sample were transferred into the breakseals. Each sample was thermolysed for 15.0 minutes at 170.0 ± 0.1°C. At 100 % reaction the maximum pressure reached would have been ~2.0 atmospheres.

The trapped alkylidenecyclopropanes (from its chiral precursor) were dissolved in 200 µl of CCl_4. Preparative separation of the alkylidenecyclopropanes was achieved on a 18.3 meter x 6.4 millimeter aluminum column packed with 20 % dimethylsulfolane on Chromosorb Paw. Column, 30°C., Injector, 150°C., TCD, 100°C., Sample size, 50 µl., Helium flow rate, 30 ml/minute. Retention times were (minutes): *trans*-2,3-dimethylmethylenecyclopropane **131** –75, *cis*-2,3-dimethylmethylenecyclopropane **132** – (121), E-2-methylethylidenecyclopropane **133** – (131), and Z-2-methylethylidenecyclopropane **134** – (137).

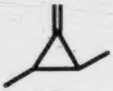
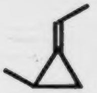
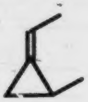
Table 13 Percentage of isomeric products from the thermolysis of pyrazolines 125 and 126 at 170.0°C (0.8-1.0 atmospheres)

Reactant	Time (minutes)	Product Composition (%)			
		 **131**	 **132**	 **133**	 **134**
 **125**	40.0	18.0 ± 0.3	37.7 ± 0.3	35.8 ± 0.2	8.5 ± 0.3
	20.0	17.1 ± 0.2	39.8 ± 0.5	34.8 ± 0.5	8.3 ± 0.3
	10.0	16.2 ± 0.3	41.5 ± 0.1	34.3 ± 0.3	8.0 ± 0.2
	5.0	16.0 ± 0.2	42.3 ± 0.4	33.6 ± 0.2	8.1 ± 0.5
 **126**	40.0	16.4 ± 0.3	10.4 ±0.9	60.4 ± 0.9	12.8 ± 0.5
	20.0	16.1 ± 0.6	11.1 ± 1.0	60.1 ± 1.0	12.7 ± 0.8
	10.0	16.0 ± 0.5	11.7 ± 0.6	59.3 ± 0.8	13.0 ± 1.0
	5.0	16.0 ± 0.9	11.5 ± 1.2	60.0 ± 1.2	13.1 ± 1.2

[a] Zero time value obtained by extrapolation.

[b] Equilibrium value,see reference 58.

Table 14 Optical rotation of MCP derived from the thermolysis of optically active *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126**[a] (15.0 min. at 170°C)

λ (nm)	 **131** 3.12 mg[b]	 **133** 6.92 mg[c]	 **134** 3.25 mg[d]
589	+0.001	-0.001	0.000
578	+0.001	-0.002	-0.001
546	+0.002	-0.001	0.000
436	+0.002	-0.003	-0.001
365	+0.004	-0.003	+0.002

[a] >95% pure as a mixture of *trans* and *cis* isomer. 4.1% *cis*. 93.4% ee.

[b] >98% isomerically pure. <5% other materials.

[c] >98% isomerically pure. <5% other materials.

[d] >98% isomerically pure. <10% other materials.

Table 15 Kinetic study of *cis*-3,5-dimethyl-4-methylene-1-pyrazoline **125** at 170°C

	Pyrazoline Composition[a]		
Time (minutes)	% **125**	% **126**	Σcts pyr/cts benzene-d$_6$
40.0	>97.0		
20.0	97.4 ± 0.6	2.6 ± 0.6	2.4 ± 0.1
10.0	97.7 ± 0.6	2.3 ± 0.6	6.3 ± 0.6
5.0	98.5 ±0.3	1.5 ± 0.3	11.6 ± 0.2
2.6	98.3 ± 0.2	1.7 ± 0.2	14.4 ± 0.2
0[b]	98.0 ± 0.1	2.0 ± 0.1	

[a] No evidence of ethylidenecyclopropanes **99** and **108** found.

[b] Original 3,5-dimethyl-4-methylenepyrazoline composition prior to thermolysis.

Table 16 Kinetic study of *trans*-3,5-dimethyl-4-methylene-1-pyrazoline **126** at 170°C

	Pyrazoline Composition[a]		
Time (minutes)	% **125**[a]	% **126**	Σctspyr/ctsbenzene d_6
40.0		>99.8	
20.0		▪	
10.0		▪	0.047 ± 0.002
5.0		▪	0.090 ± 0.004
2.0		▪	0.125 ± 0.005
0[b]		>99.8	

[a] No evidence of the *cis* pyrazoline **125** or ethylidinecyclopropanes **99** and **108** found.

[b] Original 3,5-dimethyl-4-methylenepyrazoline composition prior to thermolysis

Phenyl hydrazodicarboxylate

A modification of the method of Rabjohn[73] was used. Into a 500 ml 3-necked flask equipped with a 2-150 ml dropping funnels, a mechanical stirrer, and a thermometer was placed a solution of hydrazine monohydrate (10.8 g, 0.43 mole) in 100 ml of 95 % ethanol. After cooling to 10°C phenylchloroformate (67.3 g, 0.216 mole) was slowly added to keep the temperature ≤20°C. When half the chloroformate was added, sodium carbonate (22.8 g, 0.215 mole) dissolved in 100 ml of water was added simultaneously at a rate such that there was always an excess of formate over base. When all the reagents where added precipitate was washed off the walls with 40 ml of water. The mixture was stirred for 30 minutes at room temperature , then the precipitate was collected through filtration. Recrystallization of solid from hot ethanol and drying at 0.1 torr for 24 h gave white phenyl hydrazodicarboxylate crystals (52.4 g, 0.192 mole, 90 %). Mp 156.5-157.5.

Anal. calcd. for $C_{14}H_{12}N_2O_4$: C 61.71, H 4.44, N 10.29, O 23.51. found : C 61.59, H 4.49, N 10.25, O 23.67.

M/e (calcd. for $C_{14}H_{12}N_2O_2$, 272.0773) 272.0798.

I. r. (cm^{-1}): 3545, 3460, 3220, N-H stretch ; 1745, 1722, C=O stretch ; 1493, N-H bend.

^1H NMR spectrum ($CDCl_3$, 300 MHz) δ: 7.42 (t, J=7.9Hz, 2H), 7.25 (t, J=7.2Hz, 1H), 7.14 (d, J=7.2Hz, 2H), 9.98 (s, 2H).

^{13}C NMR spectrum (DMSO-d_6, 75.5 MHz) δ: 159.93, 155.71, 134.68, 130.67, 126.64.

Attempted synthesis of 1,2-dicarphenoxy-3,5-dimethyl-4-methylenepyrazolidine (151)

An adaption of the method of Rubottom and Chabala[53] was used. Under an argon atmosphere, sodium hydride (25 mg of 60 % in oil, 0.688 mmole, washed with 2 x 0.5 ml ether) with the aid of 3 ml ether, was added slowly to a 0°C 50 ml 3-necked flask containing phenylhydrazodicarboxylate (190 mg, 0.696 mmole) dissolved in 4 ml DME. The flask was warmed to room temperature and stirred for 30 minutes until no hydrogen gas was evolved. To this solution (cooled to 0°C) was added *rac*-3-methylene-2,4-dichloropentane (106 mg, > 90 % pure, max. of 0.691 mmole) in 2 ml dry of DME from the above reaction. After stirring for 21 h at room temperature, the reaction mixture was cooled to 0°C and sodium hydride (25 mg of 60 % in oil, 0.688 mmole) was added. Stirring was continued for 36 h at room temperature upon which water (20 ml) was slowly added to quench the reaction. The water was extracted with 6 x 20 ml of dichloromethane. After the combined extracts were dryed over sodium sulfate, the solution was concentrated at 50 torr. The concentrate contained unreacted dichloride and phenol as analyzed by TLC, ^1H NMR, and GC (6.1 m. OV101 column).

Benzyl hydrazodicarboxylate

A modification of the method of Rabjohn[73] was used. Into a 500 ml 3-necked flask equipped with a 2-150 ml dropping funnels, a mechanical stirrer, and a thermometer was placed a solution of hydrazine monohydrate (14.7 g, 0..294 mole) in 150 ml of 95 % ethanol. After cooling to 10°C benzylchloroformate (105 g, 0.615 mole) was slowly added to keep the temperature ≤20°C. When half the chloroformate was added, sodium carbonate (32 g, 0..302 mole) dissolved in 150 ml of water was added simultaneously at a rate such that there was always an excess of formate over base. When all the reagents were added, the precipitate was washed from the walls with 60 ml of water. The mixture was stirred for 30 minutes at room temperature , after which the precipitate was collected through filtration. Recrystallization of solid from hot ethanol and drying at 0.1 torr for 24 h gave white benzylhydrazodicarboxylate crystals (82.2 g, 0.273 mole, 93 %). Mp 106-107°C.

Anal. calcd. for $C_{16}H_{16}O_4N_2$: C 63.99 ; H 5.37, N 9.33, O 21.31. found : C 64.14, H 5.16, N 9.56, O 21.14.

M/e (calcd. for $C_{16}H_{16}O_4N_2$, 300.1085) 300.1107.

I. r. (cm^{-1}): 3380, 3310, N-H stretch ; 1767, 1705, C=O stretch ; 1505, N-H bend.

^1H NMR spectrum (CDCl$_3$, 200 MHz) δ: 7.33 (s, 10H), 6.66 (s, 2H), 5.14 (s, 4H)

1,2-Dicarbenzoxy-3,5-dimethyl-4-methylenepyrazolidene (150)

An adaption of the method of Rubottom and Chabala[53] was used. Under an argon atmosphere, sodium hydride (18.0 mg of 66 % in oil, 0.496 mmole) was added slowly to a 10°C 50 ml 3-necked flask containing benzyl hydrazodicarboxylate (149 mg, 0.496 mmole) dissolved in 2 ml of dry HMPA. The flask was warmed to room temperature and stirred for 30 minutes untill no hydrogen gas was evolved. To this solution was added *rac*-3-methylene-2,4-dichloropentane (75.9 mg, >98 % *rac*, > 90 % pure, max. of 0.496 mmole) in 2 ml of dry THF. After stirring for 72 h, the reaction mixture was cooled to 0°C and sodium hydride (18.0 mg of 66 % in oil, 0.496 mmole) was added. Stirring was continued for 72 h at room temperature upon which water (5ml) was slowly added to quench the reaction. The water was extracted with 3 x 10 ml of pentane. After the combined extracts were dryed over sodium sulfate, the solution was concentrated at 20 torr. Purification on a 230-400 mesh flash silica column using 3.5:1 hexane-ethyl acetate as an eluent gave a mixture of pyrazolines (58.9 mg, 0.155 mmole, min. 31 %) : *trans*-1,2-dicarbenzoxy-3,5-dimethyl-4-methylenepyrazolidine 32 %, *cis*-1,2-dicarbenzoxy-3,5-dimethyl-4-methylenepyrazolidine 8%, E-1,2-dicarbbenzoxy-3-methyl-4-ethylidenepyrazolidine 60 % by ^{1}H NMR.

trans-1,2-Dicarbenzoxy-3,5-dimethyl-4-methylenepyrazolidine :

Anal. calcd. for $C_{22}H_{24}N_2O_4$: C 69.46, H 6.36, N 7.36, O 16.82. found : C 69.35, H 6.29, N 7.21, O 17.15.

M/e (calcd. for $C_{22}H_{24}N_2O_4$, 380.1709) 380.1732.

I. r. (cm^{-1}): 1707, C=O stretch ; 1670, C=C stretch.

^{1}H NMR spectrum (CDCl$_3$, 200 MHz) δ: 5.01 (t, J=1.9Hz, 2H), 4.83 (q of t, J=6.8Hz, 1.9Hz, 2H), 1.28 (d, J=6.8Hz, 6H).

^{13}C NMR spectrum (CDCl$_3$, 75.5 MHz): 156.88, 153.27, 136.12, 128.47, 127.86, 127.69, 106.00, 67.85, 58.58, 20.61.

Cis -1,2-Dicarbenzoxy-3,5-dimethyl-4-methylenepyrazolidine :

^{1}H NMR spectrum (CDCl$_3$, 200 MHz) δ: 4.98 (t, J=1.9Hz, 2H), 4.50 (q of t (b), 2H), 1.52 (d, J=6.8Hz, 6H).

E-1,2-Dicarbenzoxy-3-methyl-4-ethylidenepyrazolidine :

^{1}H NMR spectrum (CDCl$_3$, 200 MHz) δ: 5.36 (m, 1H), (4.5-4.76 multiplets, 2H), 3.8-4.0 (m, 1H), 1.62 (m, 3H), 1.20 (d, J=6.8Hz, 3H)

Phenylthiomethyl Chloride

Using the procedure of Trost and Kunz[74] sulfuryl chloride (25.0 ml, 42.0 g, 0.311 mole) in 75 ml of dichloromethane was slowly added to a refluxing solution of thioanisole (36.0 ml, 38.1 g, 0.307 mole) dissolved in 250 ml of dichloromethane. After treating at reflux for another 2 h, the mixture was concentrated at 20 torr and then distilled using a 6 inch Vigreux column to give phenylthiomethyl chloride (44.2 g, 0.279 mole, 91 %). Bp 116-117 / 20 torr (lit bp 66°C / 0.2 torr, 103-104 / 12 torr[17]).

^{1}H NMR spectrum (CDCl$_3$, 80 MHz) δ: 7.21 (m, 5H), 4.98 (s, 2H).

3-Phenylsulfinylmethyl-2,4-pentanedione (158)

An adaption of the methodology of Paterson and Fleming was used[55]. To the silyl enol ether of acetylacetone **157** (1.04 g, 6.06 mmole), dissolved in 20 ml of dry dichloromethane and under an argon atmosphere, was added slowly phenylthiomethyl chloride (1.04 g, 6.56 mmole) in 10 ml of dry dichloromethane. After 19 h of stirring water (20 ml) was added to quench the reaction. The aqueous layer was extracted with 3 x 30 ml of dichloromethane, and the combined organic layers washed with 20 ml brine. Drying over magnesium sulphate and then concentrating at 20 torr gave mainly acetylacetone. Chromatography using 230-400 mesh silica gel and 2:1 petroleum ether (30-60°C)-ether as an eluent indicated <10 % of a mixture of 3-phenylsulfinylmethyl-2,4-pentanedione **158** and the O-alkylated phenylsulfinylmethyl enol ether of acetylacetone **159**.

3-Phenylsulfinylmethyl-2,4-pentanedione :

^{1}H NMR spectrum ($CDCl_3$, 60 MHz) δ: 7.4 (m, 5H), 3.75 (s, 2H), 2.15 (s, 6H).

M/e (calcd for $C_{12}H_{14}SO_2$, 222.0701) 222.0707.

Phenylsulfinylmethyl enol ether of acetylacetone :

^{1}H NMR spectrum ($CDCl_3$, 200 MHz) δ: 7.38 (m, 5H), 5.50 (s, 1H), 5.20 (s, 2H), 2.30 (s, 3H), 2.13 (s, 3H).

I. r. (cm^{-1}): no broad O-H stretch at >3200.

Attempted synthesis of 3-methylene-2,4-dibromopentane (162)

Under an argon atmosphere *n*-butyl lithium (6.0 ml, 1.36 M in hexane, 8.16 mmole) was slowly added to a 0°C heterogeneous mixture of methyltriphenylphosphonium bromide (2.81 g, 8.20 mmole) in 25 ml of THF. After stirring for 30 minutes, 2,4-dibromo-3-pentanone (2.00 g, 8.21 mmole) in 5 ml of THF was slowly added (to 0°C solution). A large amount of white precipitate formed immediately. The mixture was allowed to stir for 30 minutes at 0°C, then for 2 h at room temperature. The solid was removed by filtration and identified as methyltriphenylphosphonium bromide. Concentration of the solvent at 50 torr gave unreacted 2,4-dibromo-3-pentanone.

Attempted synthesis of 1,2-dicarbethoxy-3,5-dimethyl-4-pyrazolidone (163)

An adaption of the procedure of Rubottom and Chabala[53] was used. Under an argon atmosphere, sodium hydride (0.150 g, 66 % in oil, 413 mmole) was added to a 0°C solution of 1,2-dicarbethoxyhydrazine (1.05 g, 4.10 mmole) in 20 ml dry DME. After no more gas was liberated through an attached oil bubbler, the mixture was warmed to room temperature. During this time a large amount of precipitate appeared. 2,4-Dibromo-3-pentanone (0.982 g, 4.04 mmole) dissolved in 5 ml of DME was added and stirring continued for 20 h. The temperature was reduced to 0°C and sodium hydride (0.150 g, 66 % in oil, 413 mmole) was added. After stirring for a further 24 h at room temperature, water (20 ml) was introduced resulting in all precipitate dissolving. The water was extracted with 3 x 20 ml of ether and the combined ether layers washed with 20 ml brine. Drying over sodium sulfate and concentration at 20 torr gave unreacted 1,2-dicarbethoxyhydrazine and 2,4-dibromo-3-pentanone, as well as a small amount of unidentified material which stuck to a silica gel column (3:1 hexane/ethyl acetate as eluent).

Attempted synthesis of 3,5-dimethyl-4-pyrazolidone (164)

A modification of the procedure of Crawford and Tokanaga[75] was used. 3-Methylene-2,4-dibromopentane (5.00 g, 20.5 mmole) in 10 ml of absolute ethanol was added to a solution of hydrazine monohydrate (2.7 g, 54 mmole) and 5 mg EDTA in 10 ml absolute ethanol. After 90 minutes of stirring at room temperature, the solid that had developed (hydrazine hydrobromide) was removed by filtration. The solution was concentrated to

1/3 its original volume at 20 torr. ^{1}H NMR and TLC indicated that the concentrate contained no organics other than ethanol.

2,2-Bis(1'-bromoethyl)-1,3-dioxolane (166)

The procedure of Giusti and Morales[56] was used. Bromine (59.2 g, 0.370 mole) was added dropwise to a 10°C solution of 2,2-diethyl-1,3-dioxolane (24.1 g, 0.185 mole) in 75 ml of ether. The reaction mixture was stirred for 30 minutes at room temperature, then distilled to give 2,2-bis(1'-bromoethyl)-1,3-dioxolane (48.8 g, 0.169 mole, 91.5 %) as a mixture of two isomers (92:8 by ^{1}H NMR). Bp 76.5-78°C/0.1 torr (lit bp 71°C/0.01 torr).

major isomer:

^{1}H NMR spectrum (CDCl$_3$, 200 MHz) δ: 4.54 (q, J=6.9Hz, 2H), 4.29 (m, 4H), 1.72 (d, J=6.9Hz, 6H).

^{13}C NMR spectrum (CDCl$_3$, 50.3 MHz) δ: 111.26, 38.07, 37.15, 56.49, 82.18.

minor isomer:

^{1}H NMR spectrum (CDCl$_3$, 200 MHz) δ: 4.72 (q, J=7.0Hz, 2H), 4.29 (m, 4H), 1.68 (d, J=7.0Hz, 6H).

^{13}C NMR spectrum (CDCl$_3$, 50.3 MHz) δ: 111.26, 4.85, 8.87, 9.63.

Attempted syntheses of 4,2'-spiro-[1',3'-dioxolane]-1,2-dicarbethoxy-3,5-dimethylpyrazolidine (167)

1.

An adaption of the method of Rubottom and Chabala[53] was used. Under an argon atmosphere sodium hydride (0.126 g, 66 % in oil, 3.47 mmole) was introduced to 50 ml 3-necked flask (equipped with a reflux condenser) containing 1,2-dicarbethoxyhydrazine (1.042 g, 3.47 mmole) in

15 ml of HMPA. The mixture was allowed to warm to room temperature untill no hydrogen gas was being released. 2,2-Bis(1'-bromoethyl)-1,3-dioxolane (1.00 g, 3.47 mmole, 92:8 mixture of isomers) was added and stirring continued for 72 h. ^{1}H NMR indicated the presence of only starting materials; therefore, the temperature was increased to 60°C. Some reaction of the dibromide appeared to occur after another 72 h. The reaction mixture was cooled to 0°C and sodium hydride (0.127 g, 66 % in oil, 3.47 mmole) was added. The mixture was stirred at 100°C for 48 h leading to total disappearance of the dibromide. After cooling to room temperature 25 ml of water was added and this mixture was extracted with 4 x 25 ml of pentane. The extracts were dryed over magnesium sulfate and concentrated at >50 torr. The concentrate was analyzed by ^{1}H NMR and then decomposed and/or rearranged upon further purification on a 230-400 mesh flash column.

^{1}H NMR spectrum ($CDCl_3$, 200 MHz, major peaks) δ: 5.92 (d of d, J=17Hz, 11Hz, 1H), 5.50 (d of d, J=17Hz, 1.8Hz, 1H), 5.33 (d of d, J=10.8Hz, 1.8Hz, 1H)

2. Using sodium iodide

The above synthesis was retried with one modification–the addition of sodium iodide. Under an argon atmosphere sodium hydride (63.2 mg, 66 % in oil, 1.74 mmole) was introduced to 25 ml 3-necked flask (equipped with a reflux condenser) containing 1,2-dicarbethoxyhydrazine (0.522 g, 1.74 mmole) and sodium iodide (0.261 g, 1.74 mmole) in 5 ml of HMPA. The mixture was allowed to warm to room temperature till no hydrogen gas was being released. 2,2-Bis(1'-bromoethyl)-1,3-dioxolane (0.50 g, 1.74 mmole, 92:8 mixture of isomers) was added and stirring continued for 72 h. ^{1}H NMR indicated only starting materials; therefore, the temperature was increased to 50°C. Products identical to the above reaction were present in minor quantities after 72 h at the elevated temperature. Further stirring at 50°C led only to an increase of the same product.

Attempted syntheses of 4,2'-spiro-[1',3'-dioxolane]-3,5-dimethylpyrazolidine

1.

An adaption of the procedure of Crawford and Tokanaga[75] was used. Under argon, 2,2-bis(1'-bromoethyl)-1,3-dioxolane (1.00 g, 3.47 mmole) was added dropwise to a solution of hydrazine hydrate (0.60 g, 12 mmole) and EDTA (5 mg) in 2 ml of 98 % ethanol. After 48 h of stirring at room temperature no reaction had occurred. Sodium iodide (0.52 g, 3.74 mmole) was added and stirring continued for 72 h at room temperature. Since no reaction had occurred the reaction mixture was heated to a reflux. After several days only starting materials were present as indicated by TLC and ^{1}H NMR.

2.

To hydrazine monohydrate (0.40 g, 8.0 mmole) and potassium hydroxide (0.20 g, 3.5 mmole) dissolved in 5 ml of 98 % ethanol was added 2,2-bis(1'-bromoethyl)-1,3-dioxolane (1.00 g, 3.47 mmole). After 72 h stirring at room temperature no reaction had occurred, thus the temperature was increased to a reflux. After another 72 h the reaction was cooled down and 5 ml water added. This mixture was extracted with 3 x 20 ml ether; and the extracts dryed over sodium sulfate, and then concentrated at >20 torr. ^{1}H NMR indicated unreacted dibromide and products identical to that for the attempted synthesis of 4,2'-spiro-[1',3'-dioxolane]-1,2-dicarbethoxy-3,5-dimethylpyrazolidine.

Attempted synthesis of 4-hydroxy-3-methylene-2-pentanone (171)

Variations of the literature preparation of Itoh *et al*[57] were used. The best yield was obtained as follows. Under an argon atmosphere methyl vinyl ketone (1.2 ml, 14.4 mmole) was added slowly to a 0°C solution of diethyl aluminum iodide (21 ml, 1.0 M in toluene, 21 mmole) in 50 ml of dry dichloromethane. Immediately fresh acetaldehyde (1.2 ml, 21 mmole) was introduced. The mixture was stirred for 30 minutes at 0°C then diluted with 100 ml of ether. The mixture was washed with 30 ml of 1N hydrochloric acid and 20 ml of brine, then dryed over sodium sulfate. Purification on a 230-400 mesh flash silica column gave a product that was not totally pure. Maximum yield (107 mg, 0.94 mmole, 7 %).

M/e (calcd. for $C_6H_{10}O_2$, 114.0668) 114.0678.

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 5.14 (s, 1H), 5.06 (s, 1H), 4.69 (q, J=6.5Hz, 1H), 2.40 (s, 3H), 1.38 (d, J=6.5Hz, 3H).

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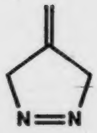
APPENDIX A - Structures



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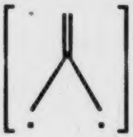

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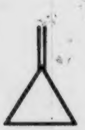

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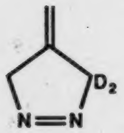

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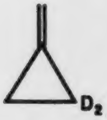

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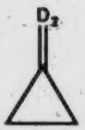

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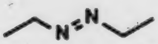

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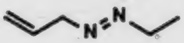

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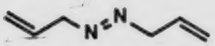

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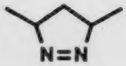

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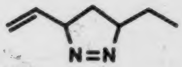

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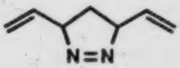

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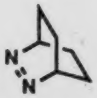

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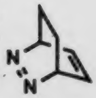

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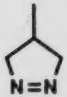

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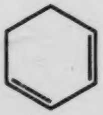

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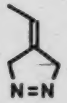

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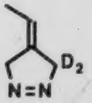

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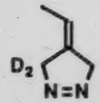

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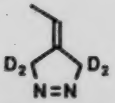

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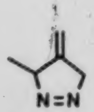

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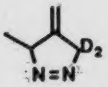

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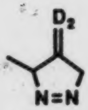

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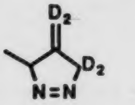

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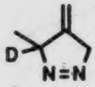

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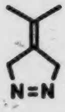

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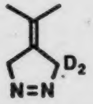

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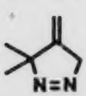

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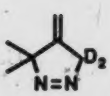

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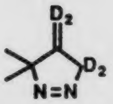

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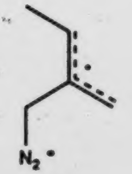

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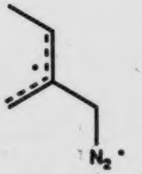

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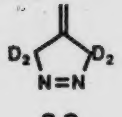

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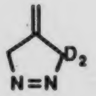

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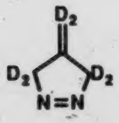

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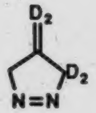

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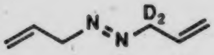

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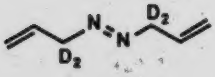

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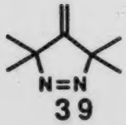

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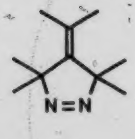

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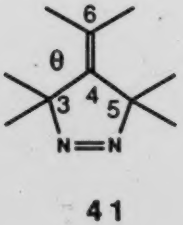

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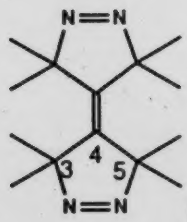

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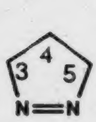

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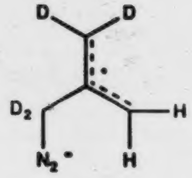

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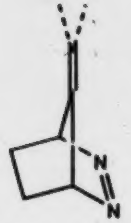

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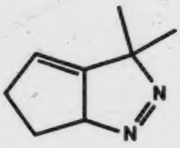

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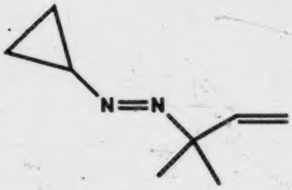

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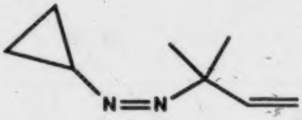

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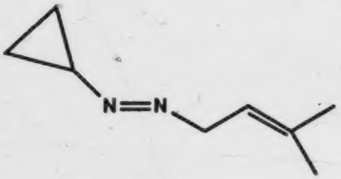

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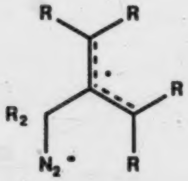

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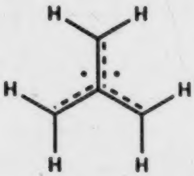

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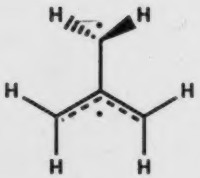

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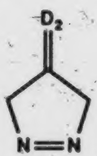

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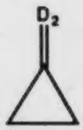

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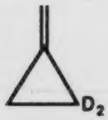

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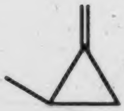

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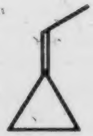

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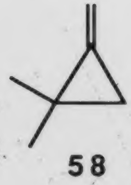

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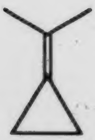

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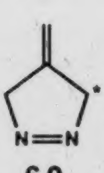

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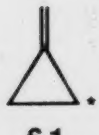

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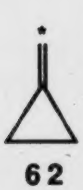

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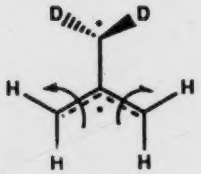

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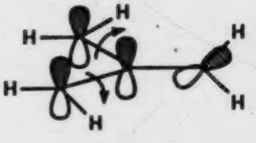

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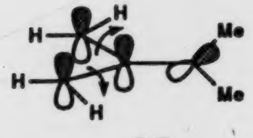

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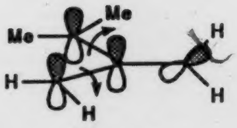

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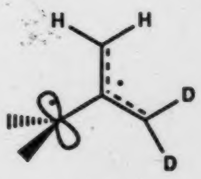

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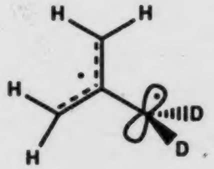

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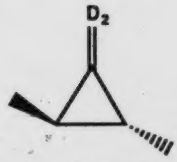

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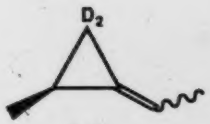

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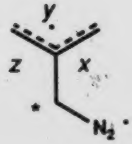

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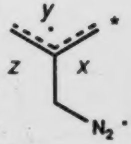

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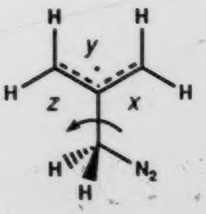

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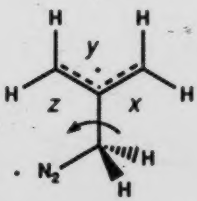

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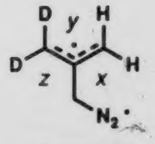

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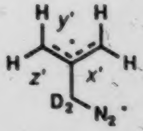

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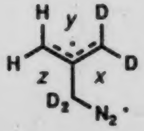

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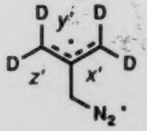

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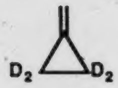

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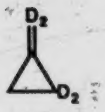

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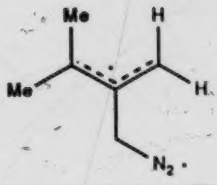

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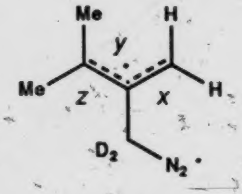

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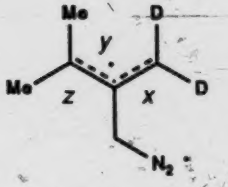

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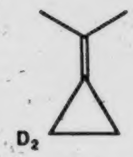

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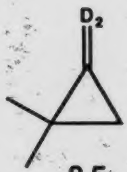

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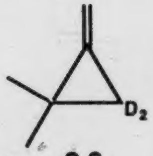

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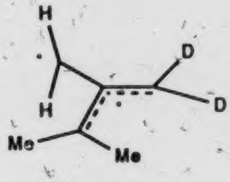

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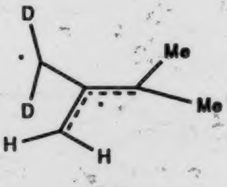

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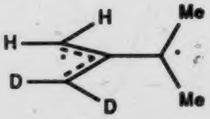

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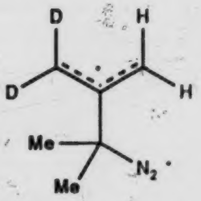

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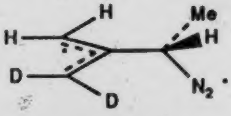

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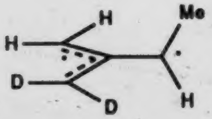

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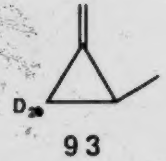

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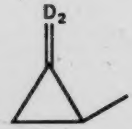

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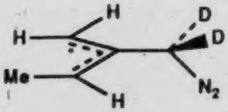

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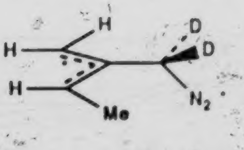

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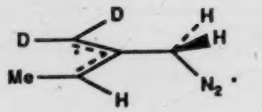

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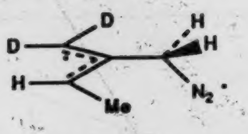

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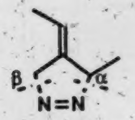

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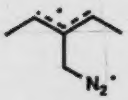

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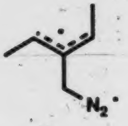

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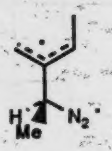

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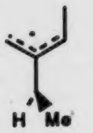

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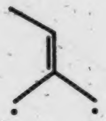

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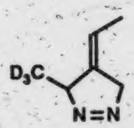

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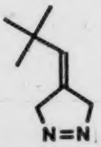

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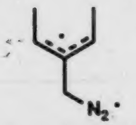

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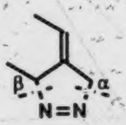

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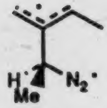

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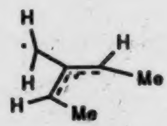

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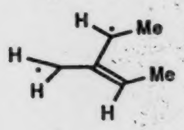

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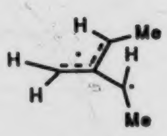

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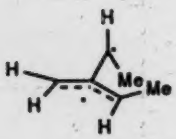
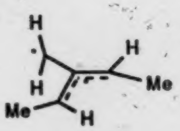


112'



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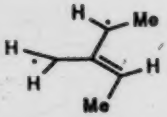

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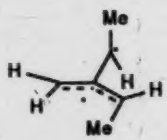

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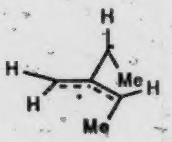

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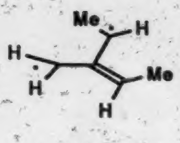

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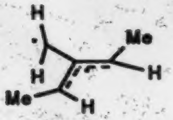

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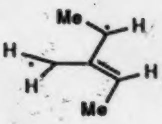

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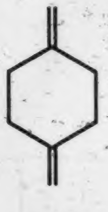

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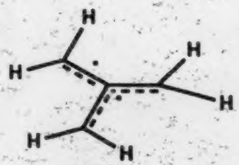
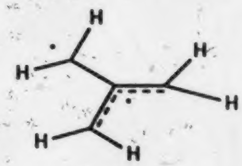
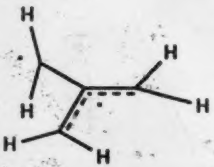


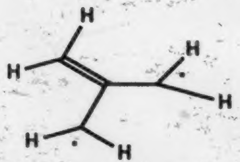
120
planar triplet
D_{3h}



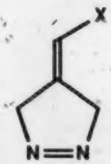
121
planar singlet
C_{2v}



122
orthogonal singlet
C_{2v} ($^1B_1$)

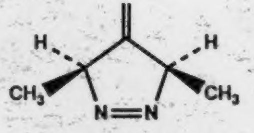


123
planar singlet
C_{2v} ($^1A_1$)

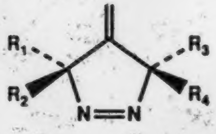


a) X=Me
b) X=F

124

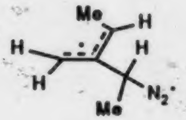


125

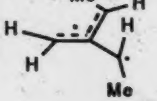


a) R_1, R_4 = H; R_2, R_3 = CH_3
b) R_1, R_4 = CH_3; R_2, R_3 = H

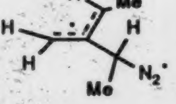
126



127



128



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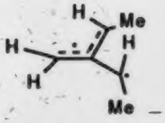

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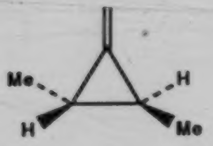
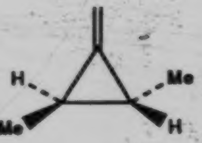
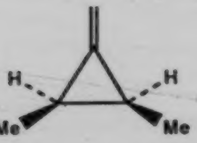


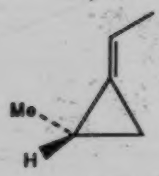
131a



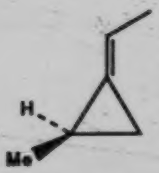
131b



132



133a



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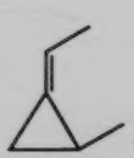

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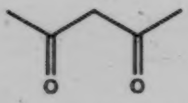

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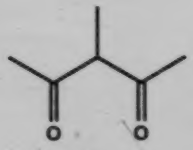

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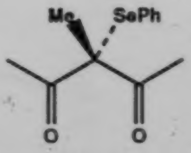

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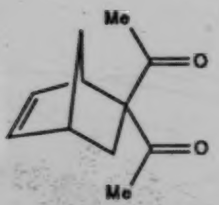
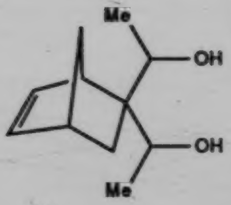


138



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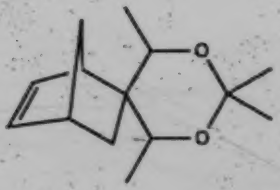

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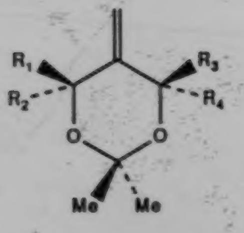
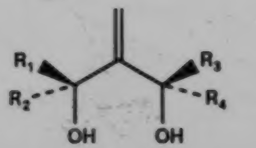


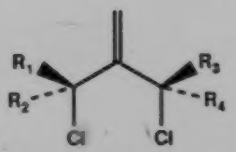
a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = H

141



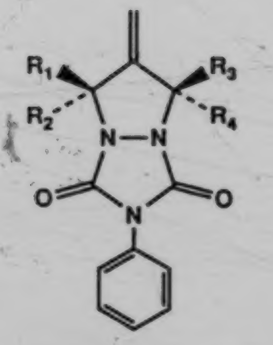
a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = h

142



a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = H

143



a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = H

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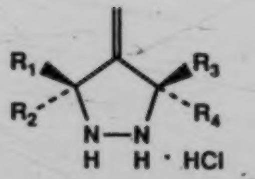

a) R_1, R_3 = Me; R_2, R_4 = H
b) R_1, R_4 = Me; R_2, R_3 = H or
R_2, R_3 = Me; R_1, R_4 = H

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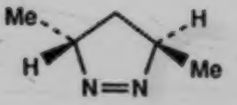

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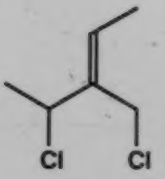

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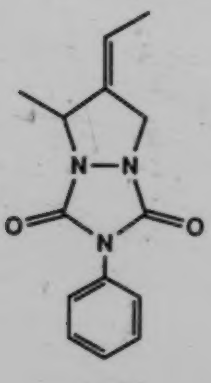

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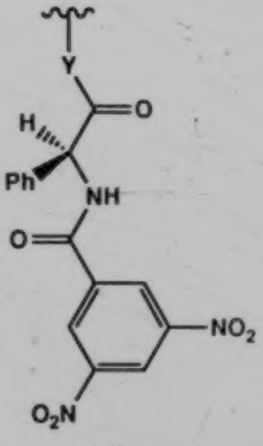

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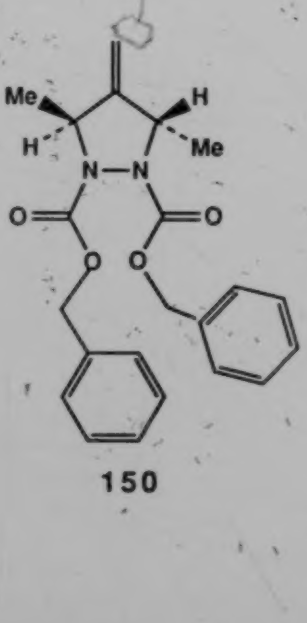

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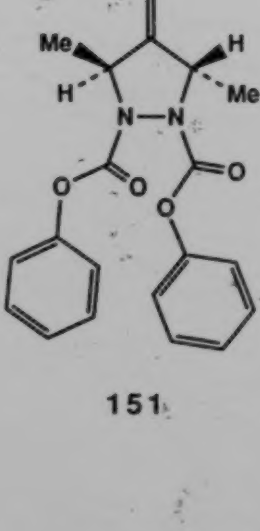

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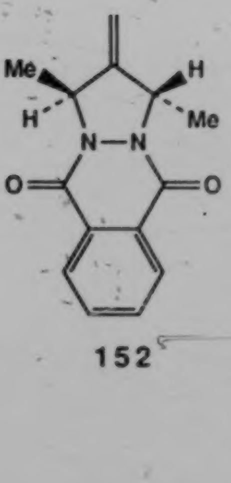

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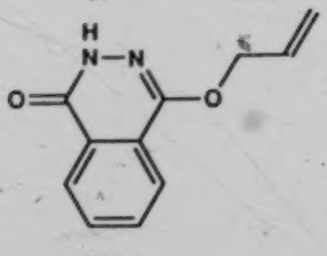

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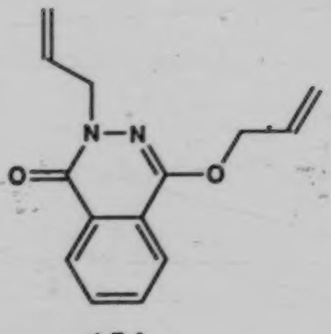

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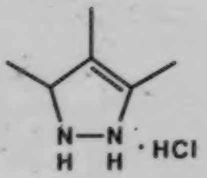

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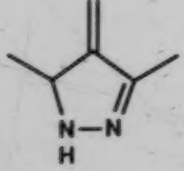

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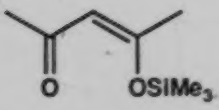

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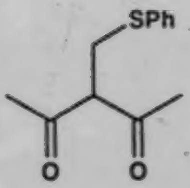

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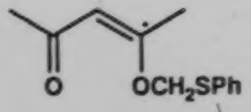

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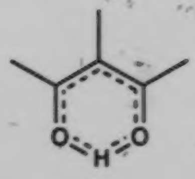

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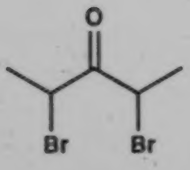

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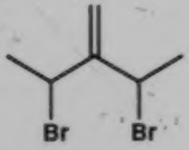

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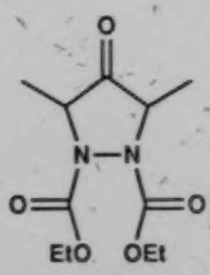

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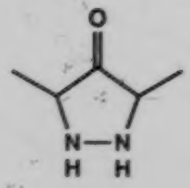

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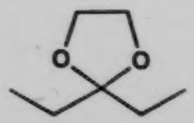

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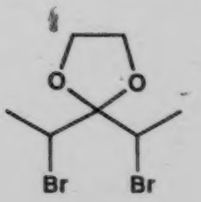

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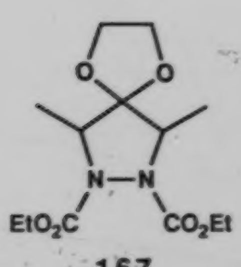

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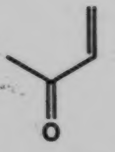

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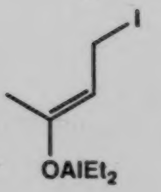

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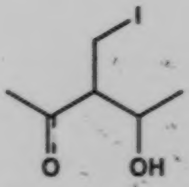

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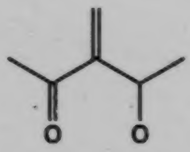

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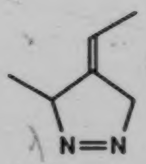

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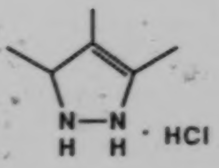

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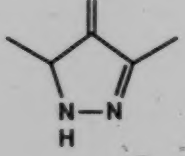

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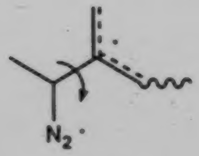

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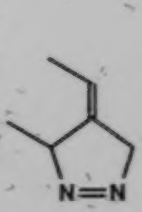

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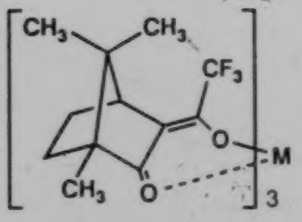

a) M = Eu

b) M = Yb

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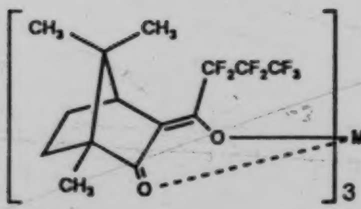

a) M = Yb, Pr
b) M = Ag

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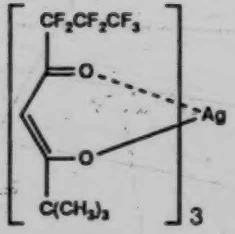

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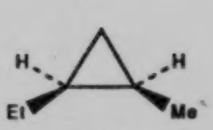

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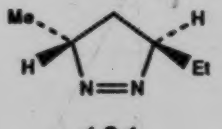

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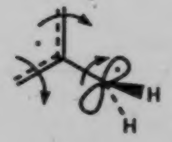

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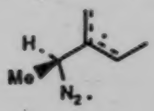

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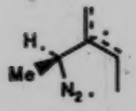

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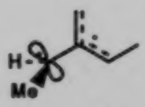

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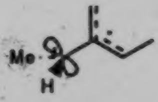

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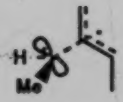

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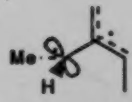

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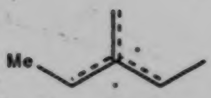

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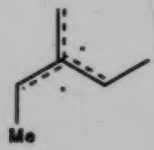

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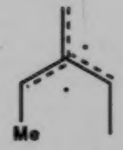

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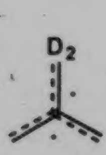

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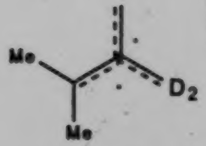

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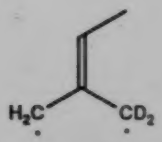

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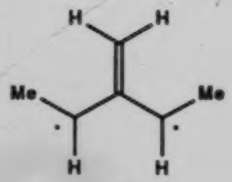

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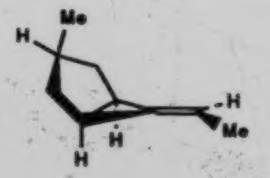

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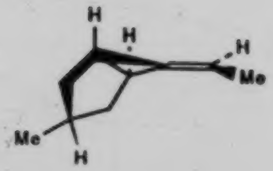

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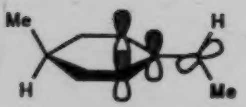

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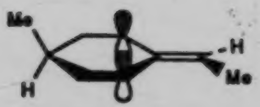

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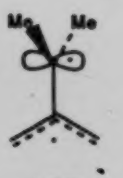

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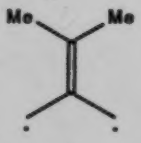

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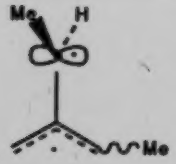

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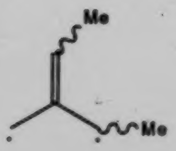

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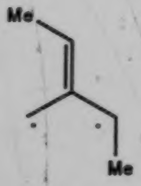

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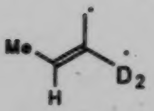

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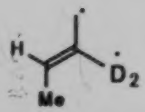

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APPENDIX B - Abbreviations

Anal.	-analysis
Calcd.	-calculated
CCl_4	-carbon tetrachloride
$CDCl_3$	-chloroform-*d*
Dibal	-diisobutyl aluminum hydride
DME	-dimethoxyethane
DMSO	-dimethylsulfoxide
EDTA	-ethylenediaminetetraacetic acid
DABCO	-diazabicyclo[2.2.2]octane
DBU	-1,5-diazabicyclo[5.4.0]undec-5-ene
DME	-dimethoxy ethane
DPG	-dinitrophenylglycine
ee	-enantiomeric excess
HMPA	-hexamethylphosphoramide
HPLC	-high performance liquid chromatography
IR	-infrared
KIE	-kinetic isotope effect
MCP	-methylenecyclopropane
m/e	-mass per electronic charge unit
NMR	nuclear magnetic resonance
Red-Al	-sodium bis-(methoxyethoxy)-aluminum hydride
THF	-tetrahydrofuran
TLC	-thin layer chromotography

For ^1H NMR spectra: b-broad, bs-broad singlet, d-doublet, m-multiplet, q-quartet, s-singlet, t-triplet.

APPENDIX C

Structure Determination Laboratory

Report on the

Complete Structure Determination and Refinement of

$C_{14}H_{15}N_3O_2$

for

J. Hiebert

EXPERIMENTAL

Data Collection

A clear, colorless crystal of $C_{14}H_{15}N_3O_2$, with the approximate dimensions of 0.15 × 0.28 × 0.42 mm, was mounted on a glass fiber with epoxy, and optically centered in the x-ray beam of an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) with a graphite crystal, incident beam monochromator.

The automatic peak search and reflection indexing programs[1] generated an orthorhombic cell. The systematic absences of $h00, h$ odd, $0k0, k$ odd, and $00\ell, \ell$ odd, and the magnitude of the unit cell volume led to the choice of space group as $P2_12_12_1$ (No. 19).[2]

The cell constants and orientation matrix were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $8.2 < \theta < 18.7°$. The unit cell parameters are given in Table 1.

The intensity data were collected with $\omega - \theta$ scans at $1.0° \mathrm{min}^{-1}$ (in θ). The scan range was varied as a function of θ to compensate for the $\alpha_1 - \alpha_2$ wavelength dispersion: ω scan width $= 0.50 + 0.347 \tan\theta$. The backgrounds for the peaks were measured by extending the scan 25% on each side of the calculated range; this gave a peak-to-background counting time ratio of 2:1. Intensity measurements were made out to a maximum 2θ of 50°. Two reflections were chosen as standard reflections, and were remeasured after every 120 min of exposure time to check on crystal and electronic stability over the course of data collection. These reflections decreased in intensity by roughly 0.3% and 0.4% over the time span of data collection. This was considered negligible, and no decay correction was employed.

Data Reduction

A total of 2975 reflections were collected, and Lorentz and polarization factors were applied:

$$I = r(S - 2B)/Lp$$

$$\sigma(I) = [r(S + 4B) + (0.04I)^2]^{1/2}/Lp$$

where r is the scan rate, S is the total scan count, B is the total background count, and Lp is the combined Lorentz and polarization factor.

Structure Solution and Refinement

The positions of all non-hydrogen atoms were evident in the best E-map generated by the direct methods program MITHRIL.[3] Adjustment[4] of atomic parameters was carried out by full-matrix least-squares refinement on F_o minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is $4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors were calculated from the analytical expression for the scattering factor curves[5]. The f' and f'' components of anomalous dispersion[6] were included in the calculations of all non-hydrogen atoms.

The hydrogen atoms were generated at idealized calculated positions by assuming a C–H bond length of 0.95Å and the appropriate sp^2 or sp^3 geometry. The hydrogen atoms on methyl groups were located by least-squares refinement of the coordinates derived from a difference Fourier map. The hydrogen atoms were then included in the calculations with fixed, isotropic Gaussian parameters 1.2 times that of the attached atom, and constrained to 'ride' on the attached atom.

The refinement of the coordinates and isotropic U's for all non-hydrogen atoms was continued to convergence. At that stage, the data were corrected for absorption by an empirical scheme based on the absorption surface (Fourier filtering) method of Walker and Stuart.[7] The maximum and minimum correction factors applied to F_o were 1.232 and 0.638. After averaging over mmm symmetry (R-merge on F is 0.031) and deleting the systematic absences, there were 2382 averaged reflections, 1085 with $I > 3\sigma(I)$, which were used in the final stages of the refinement. In the final cycle 172 parameters were refined using the 1085 observations with $I > 3\sigma(I)$, and the largest and and average shift/error ratio was less than 0.01. As a result, the final goodness-of-fit was 2.05, and

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.054$$

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.066$$

An analysis of R_2 in terms of F_o, $\sin\theta/\lambda$, various combinations of (h, k, ℓ) indicated no unusual trends. The highest peak in the final difference Fourier map has a density of 0.18(4) e Å^{-3}.

On the basis of this diffractometer data, the absolute configuration of the structure could not be unambiguously determined. Intensity data were recollected on the same crystal with an Enraf-Nonius Turbo CAD4 diffractometer with CuKα radiation, graphite monochromator, and rotating anode source (45KV, 75ma).[8] A total of 88 intensities were collected by $\theta-2\theta$ scans on both Friedel pair reflections in all four Bijvoet settings $(hk\ell, h\bar{k}\ell, hk\bar{\ell}, h\bar{k}\bar{\ell})$ of eleven enantiomer-sensitive reflections. With the atomic coordinates and displacement parameters of the structure fixed, the scale factor was determined, and the structure factor calculation was carried out on both enantiomers. For the correct structure, the agreement factors are $R_1 = 0.03949$, $R_2 = 0.05384$, and S (goodness-of-fit) = 2.561, and the enantiomer, they are $R_1 = 0.03953$, $R_2 = 0.05392$, and $S = 2.565$. While the differences are marginally significant, they are also consistent with the results obtained from the full data set collected with MoKα radiation and refined: R_1 0.0539768 vs. 0.0539776, R_2 0.06558 vs. 0.06559, and S 1.81477 vs. 1.81483. For the set of eleven reflections, the average difference in the magnitudes of F_c between Friedel pairs is roughly 0.01 e with Mo radiation and 0.07 e with Cu radiation.

Addendum to Structure Report RJC9001

Intensity data were recollected on the same crystal* with an Enraf-Nonius Turbo CAD4 diffractometer with CuKα radiation, graphite monochromator, and rotating anode source (45KV, 75ma). A total of 88 intensities were collected by θ-2θ scans on both Friedel pair reflections in all four Bijvoet settings (hkl, $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$) of eleven enantiomer–sensitive reflections. With the atomic coordinates and displacement parameters of the structure fixed, the scale factor was determined, and the structure factor calculation was carried out on both enantiomers. For the correct structure, the agreement factors are R_1 = 0.03949, R_2 = 0.05384, and goodness-of-fit = 2.561, and for the enantiomer, they are R_1 = 0.03953, R_2 = 0.05392, and GOF = 2.565. While the differences are marginally significant, they are consistent with the results obtained from the full data set collected with MoKα radiation and refined: R_1 0.0539768 vs 0.0539776, R_2 0.06558 vs 0.06559, and GOF 1.81477 vs 1.81483. For the set of 11 reflections, the average difference in the magnitudes of F_c between Friedel pairs was roughly 0.01 e with Mo radiation and 0.07 e with Cu radiation. A revised table of atomic coordinates and displacement parameters is attached.

* (-)-144b

Table 1. Experimental Details

A. Crystal Data

$C_{14}H_{15}N_3O_2$; FW = 257.29

Crystal dimensions: 0.15 × 0.28 × 0.42 mm

orthorhombic space group $P2_12_12_1$

$a = 5.069\,(1)$, $b = 11.853\,(1)$, $c = 22.480\,(1)$ Å

$V = 1350.7$ Å^3; $Z = 4$; $D_c = 1.265$ g cm^{-3}; $\mu = 0.52$ cm^{-1}

B. Full Data Set Collection and Refinement Conditions

Radiation:	Mo K_α ($\lambda = 0.7107$ Å)
Monochromator:	incident beam, graphite crystal
Take-off angle:	3.0°
Detector aperture:	2.40 mm horiz × 4.0 mm vert
Crystal-to-detector distance:	205 mm
Scan type:	$\omega - \theta$
Scan rate:	1.0°min^{-1}
Scan width:	$0.50 + 0.347 \tan\theta$
Data collection 2θ limit:	50°
Data collection index range:	$-h, -k, \pm\ell$
Number of Reflections:	2382 total, averaged; 1085 with $I > 3\sigma_I$
Observations:variables ratio:	1085:172
Agreement factors R_1, R_2, GOF:	0.054, 0.066, 2.05

References and Notes

1. The diffractometer programs are those supplied by Enraf-Nonius for operating the operating the CAD4F diffractometer; some local modifications Dr. R. G. Ball.

2. *International Tables for X-Ray Crystallography* (1969). Vol. I. Birmingham: Kynoch Press.

3. Gilmore, C. J. (1983). *MITHRIL* 83. A Multiple Solution Direct Methods Program. University of Glasgow.

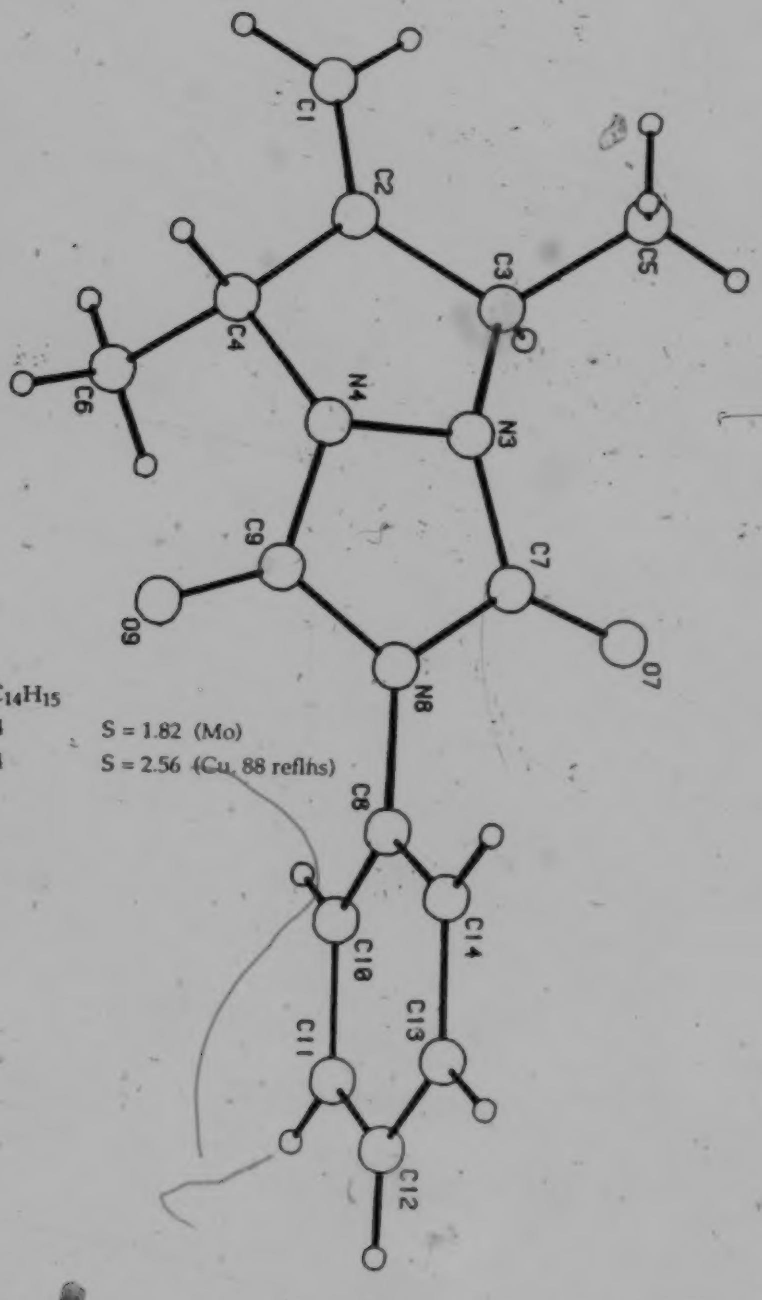
4. The computer programs used in this analysis include the Enraf–Nonius *Structure Determination Package. Version* 3 (1985, Delft, The Netherlands) adapted for a SUN Microsystems 3/160 computer, and several locally written programs by Dr. R. G. Ball.

5. *International Tables for X-Ray Crystallography* (1974). Vol. IV. Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

6. *ibid.*, Table 2.3.1.

7. Walker, N., and Stuart, D.(1983). *Acta Crystallogr.*, **A39**, 158.

8. Use of the diffractometer at the Department of Chemistry, University of Utah, made available by Dr. A. Arif.



RJC9001 $O_2N_3C_{14}H_{15}$

$R_w = 0.054$ $S = 1.82$ (Mo)

$R_w = 0.054$ $S = 2.56$ (Cu, 88 reflns)

Figure 1. Perspective view of the molecule showing the atom labelling scheme. Atoms are represented by Gaussian ellipsoids at the 30% probability level.

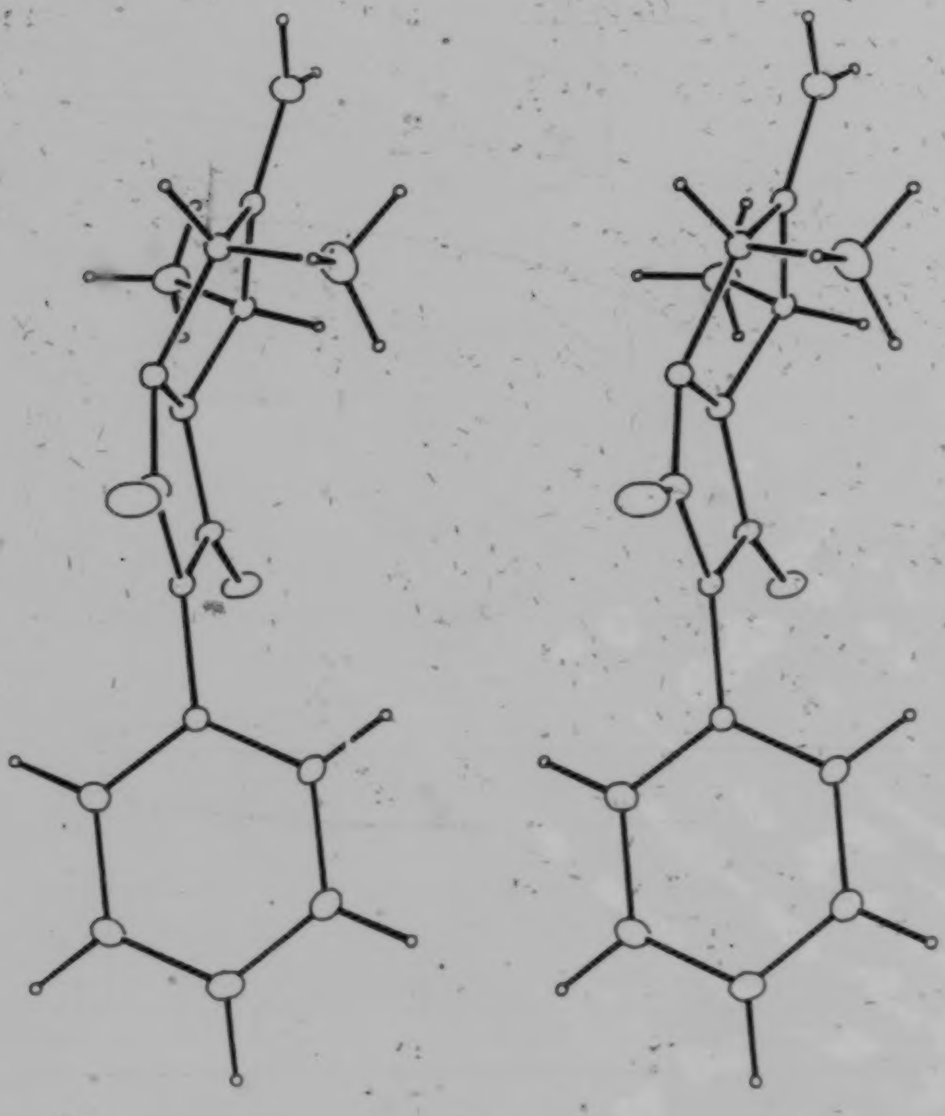


Figure 2 Stereoview of **144b**.

Table of Selected Interatomic Bond Lengths (in Å)

Atom1	Atom2	Length
C1	C2	1.312 (7)
C2	C3	1.506 (7)
C2	C4	1.483 (7)
C3	C5	1.520 (7)
C3	N3	1.475 (6)
N3	N4	1.378 (5)
N3	C7	1.375 (5)
N4	C4	1.500 (6)
N4	C9	1.365 (6)
C4	C6	1.527 (8)
C7	O7	1.197 (6)
C7	N8	1.382 (6)
N8	C9	1.365 (6)
N8	C8	1.434 (5)
C9	O9	1.225 (7)
C8	C10	1.316 (8)
C8	C14	1.337 (8)
C10	C11	1.379 (8)
C11	C12	1.305 (9)
C12	C13	1.346 (9)
C13	C14	1.402 (7)

Table of Selected Interatomic Angles (in degrees)

Atom1	Atom2	Atom3	Angle
C1	C2	C3	124.8 (5)
C1	C2	C4	124.0 (5)
C3	C2	C4	111.2 (4)
C2	C3	C5	114.6 (4)
C2	C3	N3	101.5 (4)
C5	C3	N3	111.4 (4)
C3	N3	N4	113.1 (3)
C3	N3	C7	127.2 (4)
N4	N3	C7	110.2 (4)
N3	N4	C4	109.2 (4)
N3	N4	C9	107.7 (4)
C4	N4	C9	127.2 (4)
C2	C4	N4	102.5 (4)
C2	C4	C6	113.3 (5)
N4	C4	C6	110.9 (4)
N3	C7	O7	128.2 (4)
N3	C7	N8	103.9 (4)
O7	C7	N8	127.9 (4)
C7	N8	C9	111.3 (4)
C7	N8	C8	124.3 (4)
C9	N8	C8	123.9 (4)
N4	C9	N8	106.5 (4)
N4	C9	O9	126.2 (5)
N8	C9	O9	127.4 (5)
N8	C8	C10	121.3 (5)
N8	C8	C14	119.3 (4)
C10	C8	C14	119.1 (5)
C8	C10	C11	120.6 (6)
C10	C11	C12	122.0 (6)
C11	C12	C13	118.2 (5)
C12	C13	C14	120.2 (6)
C8	C14	C13	119.6 (5)

Table of Weighted[a] Least-Squares Planes

Plane	Coefficients[b]				Defining Atoms with Deviations[c]			
1	3.2646	-7.[illegible]257	-10.1326	-11.6780				
					C2	-0.073(5)	C3	0.017(5)
					N3	0.033(4)	N4	-0.060(4)
					C4	0.113(5)		
					C1	-0.256	C5	-1.139
					C6	1.487		
2	3.7173	-1.8140	-14.8896	-11.8578				
					N3	-0.022(4)	N4	0.007(4)
					C7	0.050(5)	N8	-0.022(4)
					C9	0.026(6)		
					O7	-0.109	O9	0.088
3	3.2465	0.6838	17.2147	17.6163				
					C8	-0.020(5)	C10	0.028(7)
					C11	0.013(8)	C12	-0.023(6)
					C13	0.012(7)	C14	0.020(6)
					N8	0.023		
4	3.6701	-1.8951	-15.0824	-12.0891				
					N8	-0.032(4)	C7	0.021(5)
					C8	0.019(5)	C9	0.025(6)
					O7	0.067	O9	0.105
					C10	1.159	C14	-1.123
5	3.5102	-1.6002	-15.9298	-12.8224				
					C7	0.015(5)	O7	-0.004(4)
					N3	-0.003(4)	N8	-0.002(4)
					N4	0.110	C8	0.011
6	3.8779	-1.7642	-14.0833	-11.0399				
					C9	-0.005(6)	O9	0.001(5)
					N4	0.001(4)	N8	0.001(4)
					N3	0.038	C8	0.037
7	3.0454	-4.1387	-16.1649	-14.9273				
					N3	-0.163(4)	C7	0.099(5)
					C3	0.108(5)	N4	0.052(4)
8	3.9804	-5.4865	-9.2426	-9.1363				
					N4	-0.207(4)	C9	0.152(5)
					C4	0.133(5)	N3	0.060(4)
9	3.6996	-5.8106	-10.7082	-10.6128				
					C1	0.005(6)	C2	-0.008(5)
					C3	0.003(5)	C4	0.003(5)
					C5	-1.072	C6	1.360
					N3	-0.209	N4	-0.357

Dihedral Angles[d]

Planes	Angle	Planes	Angle	Planes	Angle	Planes	Angle
1 - 2	30.1	1 - 3	88.2	1 - 4	29.8	1 - 5	31.9
1 - 6	29.9	1 - 7	22.0	1 - 8	12.3	1 - 9	9.0
2 - 3	92.7	2 - 4	0.8	2 - 5	3.7	2 - 6	2.8
2 - 7	14.0	2 - 8	23.2	2 - 9	22.2	3 - 4	93.4
3 - 5	96.1	3 - 6	89.9	3 - 7	100.7	3 - 8	80.7
3 - 9	85.7	4 - 5	3.2	4 - 6	3.5	4 - 7	13.3
4 - 8	23.3	4 - 9	22.1	5 - 6	6.3	5 - 7	13.4
5 - 8	26.1	5 - 9	24.6	6 - 7	15.8	6 - 8	22.0
6 - 9	21.6	7 - 8	21.7	7 - 9	17.8	8 - 9	5.1

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[a] Th weights are generated from the estimated standard deviations of the atomic coordinates. The place is defined from an algorithm dervied by Hamilton, *Acta Cryst.*, 14, 185(1961).

[b] Coefficients are of the form $ax + by + cz - d = 0$, where x, y, and . are fractional crystallographic coordinates.

[c] Displacements from the least-squares plane are given in Angstroms, with the estimated standard deviations given in parentheses. Those atoms which are underlined were not included in the definition of the least-squares plane.

[d] In degrees.

Table of Torsional Angles

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C1	C2	C3	C5	52.37 (0.78)
C1	C2	C3	N3	172.51 (0.52)
C4	C2	C3	C5	-129.26 (0.51)
C4	C2	C3	N3	-9.13 (0.52)
C1	C2	C4	N4	-166.68 (0.52)
C1	C2	C4	C6	73.72 (0.68)
C3	C2	C4	N4	14.94 (0.53)
C3	C2	C4	C6	-104.66 (0.50)
C2	C3	N3	N4	-1.11 (0.49)
C2	C3	N3	C7	141.60 (0.42)
C5	C3	N3	N4	121.28 (0.44)
C5	C3	N3	C7	-96.01 (0.54)
C3	N3	N4	C4	-10.71 (0.49)
C3	N3	N4	C9	152.24 (0.41)
C7	N3	N4	C4	-138.34 (0.40)
C7	N3	N4	C9	3.20 (0.52)
C3	N3	C7	O7	-32.83 (0.78)
C3	N3	C7	N8	-149.76 (0.40)
N4	N3	C7	O7	176.42 (0.51)
N4	N3	C7	N8	-6.17 (0.49)
N3	N4	C4	C2	-15.34 (0.48)
N3	N4	C4	C6	105.90 (0.50)
C9	N4	C4	C2	-147.26 (0.48)
C9	N4	C4	C6	-26.02 (0.74)
N3	N4	C9	N8	1.27 (0.52)
N3	N4	C9	O9	-177.92 (0.55)
C4	N4	C9	N8	133.76 (0.48)
C4	N4	C9	O9	-45.43 (0.85)
N3	C7	N8	C9	7.09 (0.52)
N3	C7	N8	C8	179.80 (0.37)
O7	C7	N8	C9	-175.49 (0.52)
O7	C7	N8	C8	-2.78 (0.79)
C7	N8	C9	N4	-5.34 (0.56)
C7	N8	C9	O9	173.84 (0.56)
C8	N8	C9	N4	-178.09 (0.40)
C8	N8	C9	O9	1.09 (0.86)
C7	N8	C8	C10	-79.17 (0.64)
C7	N8	C8	C14	94.38 (0.61)
C9	N8	C8	C10	92.64 (0.66)
C9	N8	C8	C14	-93.80 (0.59)
N8	C8	C10	C11	178.63 (0.56)
C14	C8	C10	C11	5.06 (0.93)
N8	C8	C14	C13	-178.39 (0.52)
C10	C8	C14	C13	-4.69 (0.88)
C8	C10	C11	C12	-1.28 (1.13)
C10	C11	C12	C13	-2.83 (1.10)
C11	C12	C13	C14	-3.10 (1.00)
C12	C13	C14	C8	0.62 (1.01)

Table of Hydrogen Atom Coordinates ($\times 10^4$) **an** U**'s** (Å^2, $\times 10^3$).

Atom	x	y	z	U
H1	8601	9497	7824	150
H2	10802	9538	8359	150
H3	11096	7466	8944	97
H4	5065	7942	7896	102
H51	9982	9147	9402	144
H52	10029	8102	9817	144
H53	7358	8576	9591	144
H61	6198	6685	7265	182
H62	8459	6211	7658	182
H63	8812	7355	7331	182
H10	8948	3417	8460	173
H11	8558	1484	8568	213
H12	5410	716	9145	142
H13	2667	1895	9676	153
H14	2977	3868	9551	138

Table of Atomic Coordinates ($\times 10^4$) and Displacement Parameters (Å^2, $\times 10^3$).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	9371(14)	9169(4)	8168(3)	140(6)	91(3)	161(5)	-4(4)	26(6)	29(4)
C2	8440(10)	8215(4)	8376(2)	86(4)	72(3)	93(3)	16(3)	25(3)	10(3)
C3	9287(12)	7676(4)	8952(2)	64(3)	79(3)	108(4)	14(3)	2(4)	12(3)
N3	7387(8)	6738(3)	9002(1)	85(3)	68(2)	73(2)	13(2)	2(3)	2(2)
N4	5600(8)	6705(3)	8540(2)	68(3)	88(2)	96(3)	9(3)	-3(3)	28(2)
C4	6459(11)	7512(4)	8064(2)	86(4)	100(3)	82(3)	21(3)	17(3)	23(3)
C5	9155(14)	8448(4)	9491(2)	172(6)	95(3)	92(4)	-3(4)	-25(4)	-10(3)
C6	7588(16)	6878(5)	7530(3)	177(6)	162(5)	117(4)	-29(6)	29(6)	-17(5)
C7	7878(11)	5666(3)	9207(2)	96(4)	59(2)	73(3)	15(3)	4(3)	-1(2)
O7	9403(9)	5377(2)	9583(1)	161(3)	79(2)	91(2)	10(2)	-64(2)	8(2)
N8	6113(7)	5002(3)	8895(2)	62(3)	71(2)	74(2)	10(2)	-1(2)	16(2)
C8	5893(10)	3802(3)	8959(2)	66(3)	66(2)	78(3)	4(3)	2(3)	11(2)
C9	4828(11)	5611(4)	8469(2)	92(5)	93(3)	108(4)	-4(3)	-11(4)	18(3)
O9	3304(9)	5254(4)	8090(2)	166(4)	137(3)	185(3)	-31(3)	-119(3)	49(3)
C10	7571(14)	3115(4)	8698(3)	153(5)	77(3)	202(6)	32(4)	86(5)	12(4)
C11	7367(15)	1964(5)	8774(3)	162(6)	81(4)	259(7)	21(4)	88(6)	-1(5)
C12	5558(12)	1513(4)	9112(3)	106(4)	76(3)	156(5)	-3(4)	-29(5)	8(3)
C13	3930(15)	2205(4)	9412(3)	148(6)	95(3)	132(4)	-19(4)	44(5)	14(4)
C14	4110(13)	3377(4)	9336(3)	137(5)	88(3)	119(4)	-6(4)	34(4)	3(3)

The form of the displacement parameter is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Table of Root-Mean-Square Amplitudes of Displacement Parameters (in Å).

Atom	min	int'med	max	Atom	min	int'med	max
O7	0.220	0.289	0.446	C6	0.324	0.374	0.459
O9	0.234	0.347	0.560	C7	0.231	0.270	0.319
N3	0.247	0.270	0.304	C9	0.283	0.298	0.353
N4	0.238	0.273	0.347	C8	0.242	0.256	0.292
N8	0.224	0.258	0.301	C10	0.247	0.316	0.520
C1	0.279	0.360	0.429	C11	0.268	0.345	0.558
C2	0.244	0.265	0.348	C12	0.274	0.304	0.412
C3	0.235	0.287	0.337	C13	0.269	0.343	0.430
C5	0.279	0.319	0.424	C14	0.290	0.311	0.404
C4	0.256	0.267	0.363				

Table of Atomic Coordinates and Isotropic Gaussian Parameters ($\times 10^4$)

Atom	x	y	z	U_{eq}
C1	629(14)	831(4)	1832(3)	131
C2	1560(10)	1785(4)	1624(2)	84
C3	713(12)	2324(4)	1048(2)	84
C4	3541(11)	2488(4)	1936(2)	90
C5	845(14)	1552(4)	509(2)	120
C6	2412(16)	3122(5)	2470(3)	152
N3	2613(8)	3262(3)	998(1)	75
N4	4400(8)	3295(3)	1460(2)	84
C7	2122(11)	4335(3)	793(2)	76
O7	597(9)	4623(2)	417(1)	110
N8	3887(7)	4998(3)	1105(2)	69
C8	4107(10)	6198(3)	1041(2)	70
C9	5172(11)	4389(4)	1531(2)	98
O9	6696(9)	4746(4)	1910(2)	163
C10	2429(14)	6885(4)	1302(3)	144
C11	2633(15)	8036(5)	1226(3)	168
C12	4442(12)	8487(4)	888(3)	112
C13	6070(15)	7795(4)	588(3)	125
C14	5890(13)	6623(4)	664(3)	115

The equivalent isotropic Gaussian parameter U_{eq} is given by $1/3\sum_{i=1}^{3} r_i^2$, where r_i are the root-mean-square amplitudes of the anisotropic Gaussian displacement parameters, AGDP's.

Table of Anisotropic ($\times 10^4$) and Equivalent Isotropic Gaussian Displacement Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{equiv}
C1	140(6)	91(3)	161(5)	-4(4)	26(6)	29(4)	10.3(2)
C2	86(4)	72(3)	93(3)	16(3)	25(3)	10(3)	6.6(2)
C3	64(3)	79(3)	108(4)	14(3)	2(4)	12(3)	6.6(1)
C4	86(4)	100(3)	82(3)	21(3)	17(3)	23(3)	7.1(2)
C5	172(6)	95(3)	92(4)	-3(4)	-25(4)	-10(3)	9.5(2)
C6	177(6)	162(5)	117(4)	-29(6)	29(6)	-17(5)	12.0(2)
N3	85(3)	68(2)	73(2)	13(2)	2(3)	2(2)	6.0(1)
N4	68(3)	88(2)	96(3)	9(3)	-3(3)	28(2)	6.6(1)
C7	96(4)	59(2)	73(3)	15(3)	4(3)	-1(2)	6.0(1)
O7	161(3)	79(2)	91(2)	10(2)	-64(2)	8(2)	8.7(1)
N8	62(3)	71(2)	74(2)	10(2)	-1(2)	16(2)	5.4(1)
C8	66(3)	66(2)	78(3)	4(3)	2(3)	11(2)	5.5(1)
C9	92(5)	93(3)	108(4)	-4(3)	-11(4)	18(3)	7.7(2)
O9	166(4)	137(3)	185(3)	-31(3)	-119(3)	49(3)	12.9(2)
C10	153(5)	77(3)	202(6)	32(4)	86(5)	12(4)	11.4(2)
C11	162(6)	81(4)	259(7)	21(4)	88(6)	-1(5)	13.2(3)
C12	106(4)	76(3)	156(5)	-3(4)	-29(5)	8(3)	8.9(2)
C13	148(6)	95(3)	132(4)	-19(4)	44(5)	14(4)	9.9(2)
C14	137(5)	88(3)	119(4)	-6(4)	34(4)	3(3)	9.1(2)

The form of the anisotropic Gaussian displacement parameter is

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

Table of Root-Mean-Square Amplitudes of Anisotropic Gaussian Displacement Parameters (in Å)

Atom	min	int'med	max	Atom	min	int'med	max
C1	0.279	0.360	0.429	N8	0.224	0.258	0.301
C2	0.244	0.265	0.348	C8	0.242	0.256	0.292
C3	0.235	0.287	0.337	C9	0.283	0.298	0.353
C4	0.256	0.267	0.363	O9	0.234	0.347	0.560
C5	0.279	0.319	0.424	C10	0.247	0.316	0.520
C6	0.324	0.374	0.459	C11	0.268	0.345	0.558
N3	0.247	0.270	0.304	C12	0.274	0.304	0.412
N4	0.238	0.273	0.347	C13	0.269	0.343	0.430
C7	0.231	0.270	0.319	C14	0.290	0.311	0.404
O7	0.220	0.289	0.446				

Table of Atomic Coordinates and Anisotropic Gaussian Displacement Parameters ($\times 10^4$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	629(14)	831(4)	1832(3)	140(6)	91(3)	161(5)	-4(4)	26(6)	29(4)
C2	1560(10)	1785(4)	1624(2)	86(4)	72(3)	93(3)	16(3)	25(3)	10(3)
C3	713(12)	2324(4)	1048(2)	64(3)	79(3)	108(4)	14(3)	2(4)	12(3)
C4	3541(11)	2488(4)	1936(2)	86(4)	100(3)	82(3)	21(3)	17(3)	23(3)
C5	845(14)	1552(4)	509(2)	172(6)	95(3)	92(4)	-3(4)	-25(4)	-10(3)
C6	2412(16)	3122(5)	2470(3)	177(6)	162(5)	117(4)	-29(6)	29(6)	-17(5)
N3	2613(8)	3262(3)	998(1)	85(3)	68(2)	73(2)	13(2)	2(3)	2(2)
N4	4400(8)	3295(3)	1460(2)	68(3)	88(2)	96(3)	9(3)	-3(3)	28(2)
C7	2122(11)	4335(3)	793(2)	96(4)	59(2)	73(3)	15(3)	4(3)	-1(2)
O7	597(9)	4623(2)	417(1)	161(3)	79(2)	91(2)	10(2)	-64(2)	8(2)
N8	3887(7)	4998(3)	1105(2)	62(3)	71(2)	74(2)	10(2)	-1(2)	16(2)
C8	4107(10)	6198(3)	1041(2)	66(3)	66(2)	78(3)	4(3)	2(3)	11(2)
C9	5172(11)	4389(4)	1531(2)	92(5)	93(3)	108(4)	-4(3)	-11(4)	18(3)
O9	6896(9)	4746(4)	1910(2)	166(4)	137(3)	185(3)	-31(3)	-119(3)	49(3)
C10	2429(14)	6885(4)	1302(3)	153(5)	77(3)	202(6)	32(4)	86(5)	12(4)
C11	2633(15)	8036(5)	1226(3)	162(6)	81(4)	259(7)	21(4)	88(6)	-1(5)
C12	4442(12)	8487(4)	888(3)	106(4)	76(3)	156(5)	-3(4)	-29(5)	8(3)
C[illegible]	6070(15)	7795(4)	588(3)	148(6)	95(3)	132(4)	-19(4)	44(5)	14(4)
C14	5890(13)	6623(4)	664(3)	137(5)	88(3)	119(4)	-6(4)	34(4)	3(3)

The form of the anisotropic Gaussian displacement parameter is
$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Table of Hydrogen Atom Coordinates and Gaussian Parameters ($\times 10^4$)

Atom	x	y	z	U
H1	1399	503	2176	150
H2	-802	462	1641	150
H3	-1096	2534	1056	97
H4	4935	2058	2104	102
H51	18	853	598	144
H52	-29	1898	183	144
H53	2642	1424	409	144
H61	3802	3315	2735	182
H62	1541	3789	2343	182
H63	1188	2645	2669	182
H10	1052	6583	1540	173
H11	1442	8516	1432	213
H12	4590	9284	855	142
H13	7333	8105	322	153
H14	7023	6132	449	138

Table of Torsional Angles

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
C1	C2	C3	C5	-52.37 (0.78)	N3	N4	C9	N8	-1.27 (0.54)
C1	C2	C3	N3	-172.51 (0.52)	N3	N4	C9	O9	177.92 (0.53)
C4	C2	C3	C5	129.26 (0.51)	C4	N4	C9	N8	-133.76 (0.48)
C4	C2	C3	N3	9.13 (0.52)	C4	N4	C9	O9	45.43 (0.85)
C1	C2	C4	N4	166.68 (0.52)	N3	C7	N8	C9	-7.09 (0.52)
C1	C2	C4	C6	-73.72 (0.68)	N3	C7	N8	C8	-179.80 (0.42)
C3	C2	C4	N4	-14.94 (0.53)	O7	C7	N8	C9	175.49 (0.53)
C3	C2	C4	C6	104.66 (0.50)	O7	C7	N8	C8	2.78 (0.79)
C2	C3	N3	N4	1.11 (0.50)	C7	N8	C9	N4	5.34 (0.56)
C2	C3	N3	C7	-141.60 (0.42)	C7	N8	C9	O9	-173.83 (0.55)
C5	C3	N3	N4	-121.28 (0.44)	C8	N8	C9	N4	178.09 (0.41)
C5	C3	N3	C7	96.01 (0.54)	C8	N8	C9	O9	-1.08 (0.84)
C3	N3	N4	C4	-10.71 (0.49)	C7	N8	C8	C10	79.17 (0.64)
C3	N3	N4	C9	-152.24 (0.41)	C7	N8	C8	C14	-94.38 (0.61)
C7	N3	N4	C4	138.34 (0.40)	C9	N8	C8	C10	-92.64 (0.65)
C7	N3	N4	C9	-3.20 (0.52)	C9	N8	C8	C14	93.80 (0.60)
C3	N3	C7	O7	-32.83 (0.78)	N8	C8	C10	C11	-178.63 (0.55)
C3	N3	C7	N8	149.76 (0.41)	C14	C8	C10	C11	-5.06 (0.94)
N4	N3	C7	O7	-176.42 (0.50)	N8	C8	C14	C13	178.39 (0.49)
N4	N3	C7	N8	6.17 (0.49)	C10	C8	C14	C13	4.69 (0.88)
N3	N4	C4	C2	15.34 (0.48)	C8	C10	C11	C12	1.28 (1.13)
N3	N4	C4	C6	-105.90 (0.50)	C10	C11	C12	C13	2.83 (1.10)
C9	N4	C4	C2	147.26 (0.48)	C11	C12	C13	C14	-3.10 (0.99)
C9	N4	C4	C6	26.02 (0.74)	C12	C13	C14	C8	-0.62 (0.98)

Table of Observed and Calculated Structure Factor Amplitudes of All Reflections

($10F_o$, $10F_c$, and $10\sigma_F$ listed)

h	k	l	Fobs	Fcalc	Sigf
0	8	7	2176*	990	439
0	8	8	1173*	155	703
0	8	9	4095	4389	309
0	8	10	14682	15169	204
0	8	11	6248	7250	264
0	8	12	8228	8352	232
0	8	13	8634	9010	239
0	8	14	5205	6399	263
0	8	15	1156*	258	653
0	8	16	1821*	3029	469
0	8	17	2779	3348	366
0	8	18	2227*	3641	426
0	8	19	2185*	4123	435
0	8	20	1255*	1923	619
0	8	21	1306*	362	569
0	9	1	2654*	2633	416
0	9	2	8050	8587	227
0	9	3	1683*	1741	581
0	9	4	5413	5502	259
0	9	5	4659	4781	272
0	9	6	1165*	1937	711
0	9	7	-945*	65	837
0	9	8	2954	2690	383
0	9	9	-2230*	981	640
0	9	10	2995	3415	347
0	9	11	4537	5151	296
0	9	12	3692	4830	344
0	9	13	5613	6078	247
0	9	14	-1363*	1466	612
0	9	15	584*	1356	1073
0	9	16	1685*	3439	515
0	9	17	1238*	692	577
0	9	18	325*	174	1230
0	9	19	1534*	884	462
0	9	20	1470*	2308	583
0	10	0	5382	4758	268
0	10	1	1887*	1816	474
0	10	2	4674	5225	287
0	10	3	6474	6437	248
0	10	4	2555*	3488	409
0	10	5	2989	3644	368
0	10	6	1287*	296	644
0	10	7	13739	14076	195
0	10	8	7878	8548	230
0	10	9	1167*	1688	655
0	10	10	3471	3901	289
0	10	11	2300*	2701	366
0	10	12	1416*	1851	518
0	10	13	2525	3596	364
0	10	14	859*	1438	867
0	10	15	2862	2970	304
0	10	16	-1129*	1361	676
0	10	17	600*	1	1023
0	10	18	1414*	1119	521
0	11	1	6229	7055	228
0	11	2	4293	4773	274
0	11	3	6144	7087	236
0	11	4	5050	5530	256
0	11	5	3302	4204	305
0	11	6	6103	6170	221
0	11	7	2259*	2634	367
0	11	8	5917	6606	227
0	11	9	1680*	871	407
0	11	10	2587	2262	321
0	11	11	1424*	746	456
0	11	12	-1627*	1087	542
0	11	13	-348*	763	1144
0	11	14	-1762*	719	806
0	11	15	796*	703	705
0	11	16	-1410*	14	923
0	12	0	5197	5659	238
0	12	1	1008*	1488	598
0	12	2	1423*	1476	514
0	12	3	-1212*	1350	645
0	12	4	3279	3822	296
0	12	5	-410*	1162	1078
0	12	6	-1388*	450	853
0	12	7	-1467*	587	577
0	12	8	492*	663	986
0	12	9	-1374*	871	606
0	12	10	776*	1653	915
0	12	11	1907*	2549	376
0	12	12	1028*	1327	553
0	12	13	-1258*	217	936
0	13	1	2358	2044	326
0	13	2	1184*	1835	558
0	13	3	2667	2916	292
0	13	4	1971*	1758	358
0	13	5	-478*	92	963
0	13	6	1632*	1279	381
0	13	7	1330*	543	427
0	13	8	960*	405	704
0	13	9	991*	1008	601
0	13	10	688*	513	863
0	14	0	1373*	952	498
0	14	1	664*	244	795
0	14	2	1120*	858	684
1	0	1	48381	43170	99
1	0	2	121986	121225	102
1	0	3	22582	23474	117
1	0	4	18715	19786	125
1	0	5	32075	31660	124
1	0	6	49065	48432	129
1	0	7	27688	29266	138
1	0	8	18296	19232	149
1	0	9	13675	13443	165
1	0	10	14254	15345	172
1	0	11	2389*	1365	427
1	0	12	19383	18345	184
1	0	13	4002	5102	344
1	0	14	8446	8111	243
1	0	15	10292	9757	247
1	0	16	7543	7183	282
1	0	17	4044	5065	415
1	0	18	7294	7740	297
1	0	19	1253*	1087	884
1	0	20	935*	1420	1002
1	0	21	4782	5666	331
1	0	22	2059*	1693	509
1	0	23	2015*	1136	497
1	0	24	1549*	1410	593
1	0	25	1011*	3096	833
1	0	26	-2065*	332	816
1	1	-26	1795*	913	596
1	1	-25	-503*	1414	1463
1	1	-24	1570*	822	578
1	1	-23	3440	4485	392
1	1	-22	-924*	1197	1089
1	1	-21	2030*	2649	633
1	1	-20	2680*	3296	518
1	1	-19	7289	6612	291
1	1	-18	-913*	863	1055
1	1	-17	1699*	1993	776
1	1	-16	12563	12760	247
1	1	-15	1660*	1800	749
1	1	-14	5312	4590	309
1	1	-13	8836	8428	243
1	1	-12	3231	3017	375
1	1	-11	16852	15413	184
1	1	-10	12046	10989	183
1	1	-9	13598	13307	166
1	1	-8	32483	31350	80
1	1	-7	19210	20262	142
1	1	-6	41965	42370	128
1	1	-5	42835	42790	121
1	1	-4	70107	71193	112
1	1	-3	67222	67840	59
1	1	-2	57078	56976	56
1	1	-1	57292	58666	55
1	1	0	18855	18736	108
1	1	1	57322	58674	55
1	1	2	57336	56958	57
1	1	3	66855	67832	59
1	1	4	70475	71194	113
1	1	5	43076	42791	121
1	1	6	42855	42369	128
1	1	7	18748	20257	140
1	1	8	32234	31355	79
1	1	9	13027	13320	160
1	1	10	11534	10984	177
1	1	11	16550	15424	171
1	1	12	2941	3022	371
1	1	13	8403	8425	210
1	1	14	4879	4591	321
1	1	15	2157*	1806	576
1	1	16	11559	12755	233
1	1	17	-1677*	1990	737
1	1	18	-408*	864	1410
1	1	19	6404	6610	296
1	1	20	2089*	3295	562
1	1	21	1346*	2651	712
1	1	22	2253*	1198	408
1	1	23	2510*	4485	433
1	1	24	2035*	822	425
1	1	25	2170*	1414	436
1	1	26	564*	913	1017
1	2	-26	1689*	441	648
1	2	-25	1036*	934	869
1	2	-24	1239*	1317	721
1	2	-23	1096*	833	797
1	2	-22	3283	3539	473
1	2	-21	3026*	3881	491
1	2	-20	-438*	3039	1373
1	2	-19	5209	4593	377
1	2	-18	3675	2549	439
1	2	-17	9265	7563	275
1	2	-16	3295	2512	447
1	2	-15	2490*	1038	518
1	2	-14	6756	6833	284
1	2	-13	14769	13644	212
1	2	-12	12392	10750	208
1	2	-11	15767	13966	188
1	2	-10	12825	11030	184
1	2	-9	12609	12818	172
1	2	-8	7079	6597	189
1	2	-7	38007	39117	75

h	k	l	Fobs	Fcalc	Sigf
1	2	-6	30449	30551	132
1	2	-5	42101	43705	124
1	2	-4	54983	57256	117
1	2	-3	13631	14194	69
1	2	-2	41399	42499	61
1	2	-1	13266	12722	122
1	2	0	51732	53689	109
1	2	1	13248	12725	126
1	2	2	41571	42504	62
1	2	3	13747	14180	70
1	2	4	55584	57258	118
1	2	5	42426	43709	124
1	2	6	30239	30555	132
1	2	7	37852	39121	75
1	2	8	6777	6600	183
1	2	9	12412	12806	166
1	2	10	12295	11038	173
1	2	11	15069	13970	183
1	2	12	11520	10749	194
1	2	13	13831	13645	206
1	2	14	6579	6833	268
1	2	15	-528*	1040	1141
1	2	16	2414*	2509	514
1	2	17	8645	7557	252
1	2	18	2235*	2547	617
1	2	19	4603	4589	327
1	2	20	1816*	3038	599
1	2	21	2453*	3880	512
1	2	22	2713*	3541	441
1	2	23	1294*	833	636
1	2	24	-1970*	1318	715
1	2	25	1863*	934	483
1	2	26	-1644*	442	852
1	3	-25	-1980*	564	792
1	3	-24	-1219*	1978	1067
1	3	-23	1965*	2229	577
1	3	-22	-2580*	1373	584
1	3	-21	4549	4741	363
1	3	-20	4447	4952	402
1	3	-19	3908	3032	404
1	3	-18	3679	3566	482
1	3	-17	2790*	2040	575
1	3	-16	1352*	1857	922
1	3	-15	6042	6489	345
1	3	-14	6269	5395	301
1	3	-13	5244	4583	309
1	3	-12	9671	8353	230
1	3	-11	15548	15460	192
1	3	-10	7531	7485	208
1	3	-9	26323	25284	163
1	3	-8	12072	12163	172
1	3	-7	6817	7423	182
1	3	-6	22478	22565	140
1	3	-5	6145	6854	170
1	3	-4	6356	6691	167
1	3	-3	19697	19972	126
1	3	-2	32014	34182	121
1	3	-1	29388	30334	120
1	3	0	7025	7704	158
1	3	1	29878	30334	122
1	3	2	32565	34181	124
1	3	3	20164	19975	130
1	3	4	6404	6679	172
1	3	5	6671	6854	167
1	3	6	22175	22570	141
1	3	7	7023	7422	186
1	3	8	12276	12159	160
1	3	9	25605	25286	163
1	3	10	7336	7479	208
1	3	11	14636	15463	186
1	3	12	9506	8358	212
1	3	13	4532	4582	324
1	3	14	5633	5394	291
1	3	15	5863	6486	307
1	3	16	2600*	1860	458
1	3	17	2895*	2038	486
1	3	18	3222	3562	479
1	3	19	2799*	3033	475
1	3	20	4307	4952	312
1	[illegible]	21	3875	4739	322
1	3	22	1953*	1373	453
1	3	23	1483*	2226	562
1	3	24	526*	1978	969
1	3	25	1541*	564	546
1	4	-25	3250	2209	437
1	4	-24	2452*	1832	499
1	4	-23	2321*	1807	537
1	4	-22	848*	1764	972
1	4	-21	4180	3283	357
1	4	-20	3367	2412	390
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1	4	-17	4654	4662	390
1	4	-16	4547	3804	406
1	4	-15	5352	4348	363
1	4	-14	4924	4081	335
1	4	-13	7943	7536	260
1	4	-12	8208	7721	244
1	4	-11	7617	7606	245
1	4	-10	12878	12482	192
1	4	-9	15055	14841	180
1	4	-8	4766	4104	243
1	4	-7	16241	16152	159
1	4	-6	11853	12096	161
1	4	-5	5702	6100	193
1	4	-4	6793	6842	171
1	4	-3	31437	31866	74
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1	4	1	7139	7079	161
1	4	2	30515	29621	135
1	4	3	31711	31873	76
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1	4	5	6053	6096	186
1	4	6	12265	12099	160
1	4	7	15649	16150	163
1	4	8	4670	4107	241
1	4	9	14801	14849	183
1	4	10	12371	12484	198
1	4	11	7681	7603	223
1	4	12	7631	7725	236
1	4	13	7882	7536	242
1	4	14	4524	4078	340
1	4	15	4456	4348	382
1	4	16	3663	3807	439
1	4	17	3876	4664	396
1	4	18	2078*	1731	514
1	4	19	3057	2716	396
1	4	20	2823	2412	356
1	4	21	3532	3281	301
1	4	22	-1265*	1764	940
1	4	23	-1098*	1807	1128
1	4	24	649*	1833	894
1	4	25	2503*	2207	428
1	5	-24	2023*	1030	549
1	5	-23	0*	1516	1906
1	5	-22	1853*	1757	623
1	5	-21	2982	2413	430
1	5	-20	3218	2877	457
1	5	[illegible]	434*	1076	1341
1	5	-18	1156*	972	899
1	5	-17	3295*	3916	534
1	5	-16	3541	2903	448
1	5	-15	1754*	1041	718
1	5	-14	4473	3331	390
1	5	-13	1846*	1755	693
1	5	-12	5507	4613	300
1	5	-11	8030	7042	255
1	5	-10	10152	9705	217
1	5	-9	10906	10366	204
1	5	-8	16062	16289	179
1	5	-7	6039	6750	225
1	5	-6	10352	10485	178
1	5	-5	10182	10195	168
1	5	-4	5377	5298	201
1	5	-3	11440	11711	158
1	5	-2	5332	5609	197
1	5	-1	4270	3778	213
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1	5	1	3977	3772	235
1	5	2	5641	5617	195
1	5	3	11580	11715	161
1	5	4	5526	5305	216
1	5	5	10270	10189	180
1	5	6	10344	10477	185
1	5	7	6634	6751	204
1	5	8	15803	16294	181
1	5	9	10816	10376	193
1	5	10	9808	9704	217
1	5	11	7861	7040	232
1	5	12	5004	4617	308
1	5	13	2631*	1753	466
1	5	14	3034*	3332	483
1	5	15	561*	1040	1231
1	5	16	2879*	2898	448
1	5	17	3869	3917	377
1	5	18	672*	973	955
1	5	19	1829*	1076	518
1	5	20	2672*	2876	411
1	5	21	2727	2413	377
1	5	22	729*	1757	817
1	5	23	823*	1516	809
1	5	24	1670*	1030	429
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1	6	-22	1054*	2113	950
1	6	-21	1038*	625	871
1	6	-20	2613*	2752	495
1	6	-19	1045*	1368	941
1	6	-18	4543	4473	366
1	6	-17	3550	3396	440
1	6	-16	8098	7749	289
1	6	-15	1853*	2745	685
1	6	-14	3550	3334	444
1	6	-13	3299	3030	477
1	6	-12	5036	4121	319

h	k	l	Fobs	Fcalc	Sigf
1	6	-11	4484	4604	347
1	6	-10	12229	11621	224
1	6	-9	11043	10001	216
1	6	-8	7368	7836	233
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1	6	-6	18748	19465	179
1	6	-5	11694	12051	182
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1	6	-2	20043	19844	162
1	6	-1	15233	15681	165
1	6	0	11223	9827	171
1	6	1	15529	15681	166
1	6	2	20315	19836	167
1	6	3	17964	17156	95
1	6	4	15547	15519	179
1	6	5	12245	12055	185
1	6	6	19819	19465	182
1	6	7	14611	14247	187
1	6	8	7769	7840	231
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1	6	11	4663	4608	328
1	6	12	3921	4118	380
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1	6	14	3549	3338	408
1	6	15	1582*	2745	699
1	6	16	7453	7746	256
1	6	17	3481	3397	352
1	6	18	4318	4475	280
1	6	19	1770*	1367	476
1	6	20	1703*	2751	530
1	6	21	1018*	626	676
1	6	22	0*	2113	1844
1	6	23	-1252*	309	961
1	7	-22	-1773*	1795	882
1	7	-21	428*	975	1187
1	7	-20	594*	1425	1156
1	7	-19	2772*	2608	442
1	7	-18	3350	3703	441
1	7	-17	5495	6048	321
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1	7	-15	3728	3372	396
1	7	-14	8215	7451	265
1	7	-13	6919	7366	296
1	7	-12	5996	5215	328
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1	7	2	7616	7253	218
1	7	3	11498	10932	200
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1	7	8	12373	12099	214
1	7	9	3121	2906	441
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1	7	12	6138	5216	285
1	7	13	6700	7367	276
1	7	14	6997	7453	273
1	7	15	2725*	3374	450
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1	7	17	4166	6046	308
1	7	18	2919	3700	372
1	7	19	2498	2606	369
1	7	20	939*	1424	738
1	7	21	1340*	975	514
1	7	22	-1982*	1795	812
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1	8	-20	952*	1592	916
1	8	-19	-1634*	736	885
1	8	-18	-1275*	983	958
1	8	-17	2449*	2610	496
1	8	-16	3652	3892	370
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1	8	-8	4630	3918	310
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1	8	3	2668*	3874	504
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1	8	5	8058	7726	259
1	8	6	4085	3642	344
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1	8	9	7002	6160	252
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1	8	11	6650	6761	289
1	8	12	6205	6273	303
1	8	13	4328	4639	334
1	8	14	4424	4425	282
1	8	15	3901	4475	310
1	8	16	2462*	3890	410
1	8	17	1000*	2609	769
1	8	18	-2045*	985	712
1	8	19	1442*	735	478
1	8	20	1005*	1591	691
1	8	21	1854*	1201	395
1	9	-20	1936*	262	563
1	9	-19	-1612*	585	882
1	9	-18	2928	3222	432
1	9	-17	-692*	317	1253
1	9	-16	1683*	2501	592
1	9	-15	2737*	3334	425
1	9	-14	2586	1690	371
1	9	-13	7078	7421	261
1	9	-12	-1478*	1743	865
1	9	-11	6249	6030	279
1	9	-10	5759	5615	289
1	9	-9	13510	13024	227
1	9	-8	1329*	1414	760
1	9	-7	4487	4618	341
1	9	-6	3604	3663	399
1	9	-5	6954	7153	269
1	9	-4	11301	10901	227
1	9	-3	1535*	2852	730
1	9	-2	3468	3689	398
1	9	-1	2832*	2225	436
1	9	0	2204*	743	472
1	9	1	1978*	2225	569
1	9	2	4009	3690	318
1	9	3	3580	2851	368
1	9	4	11391	10901	226
1	9	5	7172	7150	262
1	9	6	3424	3665	447
1	9	7	4888	4618	320
1	9	8	3217	1409	371
1	9	9	12922	13028	226
1	9	10	5521	5614	291
1	9	11	5481	6031	283
1	9	12	839*	1745	874
1	9	13	5874	7419	271
1	9	14	2101*	1691	375
1	9	15	2371*	3312	377
1	9	16	599*	2502	899
1	9	17	688*	316	763
1	9	18	2404	3222	369
1	9	19	-1907*	586	790
1	9	20	377*	201	1021
1	10	-18	1070*	605	844
1	10	-17	2702*	1771	429
1	10	-16	-1321*	1921	1046
1	10	-15	1027*	2621	774
1	10	-14	1954*	1198	403
1	10	-13	1704*	1172	574
1	10	-12	-1144*	746	981
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1	10	-10	4185	4099	302
1	10	-9	4381	4441	303
1	10	-8	2829	[illegible]	377
1	10	-7	5700	5841	277
1	10	-6	7945	7946	238
1	10	-5	7981	7758	244
1	10	-4	4454	4699	309
1	10	-3	3858	3655	351
1	10	-2	2844	3316	409
1	10	-1	5953	5841	275
1	10	0	6791	6435	250
1	10	1	5890	5839	277
1	10	2	2656*	3312	458
1	10	3	3985	3651	317
1	10	4	4643	4700	309
1	10	5	8130	7762	248
1	10	6	7755	7944	249
1	10	7	5486	5850	270
1	10	8	2636*	2350	427
1	10	9	4228	4444	303
1	10	10	3093	4103	367
1	10	11	3971	5055	281
1	10	12	351*	745	1004
1	10	13	1465*	1173	509

h	k	l	Fobs	Fcalc	Sigf
1	10	14	1527*	1198	474
1	10	15	1734*	2621	437
1	10	16	1713*	1921	441
1	10	17	1855*	1770	434
1	10	18	-897*	606	1210
1	11	-16	1603*	177	625
1	11	-15	700*	195	932
1	11	-14	1027*	1451	756
1	11	-13	2037*	867	398
1	11	-12	-1764*	295	770
1	11	-11	1520*	1594	580
1	11	-10	3113	3192	337
1	11	-9	3336	3604	350
1	11	-8	4174	3889	271
1	11	-7	970*	1462	697
1	11	-6	3135	3595	356
1	11	-5	1801*	1524	515
1	11	-4	4390	4556	288
1	11	-3	4475	5262	279
1	11	-2	1046*	953	703
1	11	-1	6534	7181	251
1	11	0	3170	2544	339
1	11	1	6908	7185	230
1	11	2	-999*	954	976
1	11	3	5088	5263	257
1	11	4	4856	4552	275
1	11	5	1381*	1525	562
1	11	6	3305	3594	347
1	11	7	1210*	1462	599
1	11	8	3315	3891	355
1	11	9	4035	3603	262
1	11	10	1764*	3191	546
1	11	11	2052*	1594	411
1	11	12	1269*	296	502
1	11	13	897*	866	645
1	11	14	1282*	1451	581
1	11	15	0*	193	1949
1	11	16	0*	177	1783
1	12	-13	2122*	1976	478
1	12	-12	955*	1152	699
1	12	-11	1808*	1091	413
1	12	-10	638*	1243	889
1	12	-9	960*	1233	715
1	12	-8	-1386*	1262	986
1	12	-7	1073*	506	649
1	12	-6	1986*	1856	426
1	12	-5	-829*	1218	1131
1	12	-4	1783*	1736	476
1	12	-3	505*	1920	991
1	12	-2	3964	3763	296
1	12	-1	-2109*	660	666
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1	12	1	0*	657	1742
1	12	2	3470	3763	341
1	12	3	946*	1922	720
1	12	4	1953*	1736	452
1	12	5	1282*	1220	554
1	12	6	708*	1859	853
1	12	7	611*	508	869
1	12	8	497*	1262	896
1	12	9	2121*	1234	350
1	12	10	1876*	1242	381
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1	12	13	1202*	1977	669
1	13	-9	-899*	700	1137
1	13	-8	1950*	1112	410
1	13	-7	915*	544	731
1	13	-6	-1342*	373	909
1	13	-5	513*	1670	944
1	13	-4	1439*	797	462
1	13	-3	620*	741	760
1	13	-2	-2442*	525	651
1	13	-1	3358	2564	273
1	13	0	-1926*	413	798
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1	13	2	1007*	525	617
1	13	3	-999*	739	1117
1	13	4	1385*	795	494
1	13	5	1606*	1670	499
1	13	6	1252*	373	553
1	13	7	1152*	543	563
1	13	8	1098*	1111	631
1	13	9	2013*	701	362
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2	0	3	19350	18803	153
2	0	4	1591*	2371	585
2	0	5	25184	25163	165
2	0	6	7983	7959	219
2	0	7	20710	21954	183
2	0	8	8950	10076	230
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2	0	10	16400	15750	215
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2	0	16	4453	4108	413
2	0	17	1717*	930	852
2	0	18	4794	5417	357
2	0	19	2588*	2248	516
2	0	20	4300	5064	353
2	0	21	1201*	1748	802
2	0	22	-2115*	268	732
2	0	23	1837*	2547	674
2	0	24	902*	940	891
2	0	25	1469*	1796	726
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2	1	-24	-1131*	1135	1093
2	1	-23	1570*	1634	715
2	1	-22	2049*	1338	651
2	1	-21	4066	4603	380
2	1	-20	2120*	2160	680
2	1	-19	2638*	3330	628
2	1	-18	6292	6293	366
2	1	-17	6622	6436	364
2	1	-16	8541	7576	339
2	1	-15	7225	7525	373
2	1	-14	9513	9183	307
2	1	-13	4298	4329	456
2	1	-12	11833	10070	266
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2	1	0	8205	8061	174
2	1	1	8275	8386	171
2	1	2	4052	4280	256
2	1	3	17952	17919	150
2	1	4	8954	9119	179
2	1	5	19259	19939	91
2	1	6	3648	4440	338
2	1	7	29738	29059	96
2	1	8	19776	19328	181
2	1	9	2944	3209	450
2	1	10	13959	13480	211
2	1	11	17280	16886	214
2	1	12	11316	10075	239
2	1	13	4103	4330	430
2	1	14	8684	9180	273
2	1	15	6786	7523	314
2	1	16	8129	7574	301
2	1	17	5829	6437	348
2	1	18	5870	6296	301
2	1	19	2955	3329	450
2	1	20	2148*	[illegible]	545
2	1	21	4073	4604	309
2	1	22	1295*	[illegible]	735
2	1	23	1166*	[illegible]	714
2	1	24	561*	1135	1063
2	1	25	-734*	541	1370
2	2	-24	-508*	736	1422
2	2	-23	1775*	1383	638
2	2	-22	-966*	558	1116
2	2	-21	3228*	3296	502
2	2	-20	2653*	3016	558
2	2	-19	5875	6185	366
2	2	-18	3755	2455	479
2	2	-17	9375	9068	313
2	2	-16	1852*	1302	914
2	2	-15	9228	8495	299
2	2	-14	5053	5370	440
2	2	-13	11087	9502	262
2	2	-12	8060	[illegible]	298
2	2	-11	6381	[illegible]	311
2	2	-10	8705	8892	247
2	2	-9	18514	16649	196
2	2	-8	12677	12563	197
2	2	-7	14186	15303	182
2	2	-6	1018*	2071	753
2	2	-5	39927	40363	155
2	2	-4	5652	5841	232
2	2	-3	11135	10980	170
2	2	-2	17698	18372	156
2	2	-1	11525	11745	167
2	2	0	19067	19537	156
2	2	1	11385	11750	168
2	2	2	17283	18363	152
2	2	3	10483	10979	165
2	2	4	5846	5845	211
2	2	5	39596	40371	156
2	2	6	1194*	2059	701
2	2	7	14599	15306	181
2	2	8	12408	12562	197
2	2	9	18817	16652	193
2	2	10	8710	889	232

h	k	l	Fobs	Fcalc	Sigf
2	2	11	5717	5626	315
2	2	12	7688	7998	276
2	2	13	10192	9498	264
2	2	14	6043	5368	336
2	2	15	7893	8494	304
2	2	16	-915*	1303	1097
2	2	17	8713	9069	288
2	2	18	2460*	2457	550
2	2	19	5165	6186	306
2	2	20	2238*	3016	593
2	2	21	2687*	3296	450
2	2	22	-2367*	557	662
2	2	23	-1488*	1383	942
2	2	24	1074*	735	762
2	3	-24	-1704*	1196	849
2	3	-23	-1120*	294	978
2	3	-22	1341*	1621	849
2	3	-21	1851*	1929	691
2	3	-20	2272*	991	562
2	3	-19	5348	5606	374
2	3	-18	5292	5845	390
2	3	-17	3690	3523	529
2	3	-16	5225	5242	398
2	3	-15	3217*	2982	550
2	3	-14	1663*	2160	938
2	3	-13	3017*	2771	537
2	3	-12	5476	4925	371
2	3	-11	9500	7822	246
2	3	-10	7485	7560	267
2	3	-9	16603	16009	205
2	3	-8	19669	19180	190
2	3	-7	24274	23770	179
2	3	-6	2283*	1579	435
2	3	-5	20187	20775	167
2	3	-4	21497	21591	165
2	3	-3	3030	2467	328
2	3	-2	7671	7489	198
2	3	-1	17457	16511	167
2	3	0	33689	33985	159
2	3	1	16629	16505	169
2	3	2	7457	7491	209
2	3	3	2173*	2472	466
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2	3	5	20226	20778	169
2	3	6	1568*	1584	571
2	3	7	24818	23775	175
2	3	8	19234	19179	190
2	3	9	16295	16008	197
2	3	10	7184	7557	264
2	3	11	8255	7816	270
2	3	12	4863	4922	371
2	3	13	1779*	2770	762
2	3	14	3309	2158	460
2	3	15	3165*	2982	514
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2	3	17	3406	3523	503
2	3	18	4510	5843	414
2	3	19	4446	5606	386
2	3	20	1829*	990	568
2	3	21	-1780*	1927	850
2	3	22	2393*	1622	384
2	3	23	987*	292	710
2	3	24	-1541*	1197	873
2	4	-24	1653*	1475	830
2	4	-23	-1684*	1515	892
2	4	-22	1693*	723	698
2	4	-21	3864	3766	417
2	4	-20	1106*	1037	884
2	4	-19	3092*	2840	524
2	4	-18	4948	4240	393
2	4	-17	7045	7017	312
2	4	-16	2713*	2861	614
2	4	-15	6826	6343	322
2	4	-14	3899	3074	453
2	4	-13	750*	846	1304
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2	4	-10	1289*	153	797
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2	4	-7	9355	9390	213
2	4	-6	7094	7094	231
2	4	-5	16244	15927	184
2	4	-4	6818	6425	225
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2	4	5	16930	15914	185
2	4	6	7309	7102	243
2	4	7	9214	9386	227
2	4	8	8488	8684	236
2	4	9	7729	6962	236
2	4	10	1624*	152	656
2	4	11	5201	4574	308
2	4	12	4454	4141	385
2	4	13	-1570*	848	727
2	4	14	2146*	3073	642
2	4	15	5783	6346	354
2	4	16	1129*	2860	984
2	4	17	5978	7016	332
2	4	18	3831	4239	401
2	4	19	3073	2837	447
2	4	20	-1489*	1038	845
2	4	21	3325	3764	381
2	4	22	-495*	722	1369
2	4	23	1495*	1514	672
2	4	24	-901*	1475	1171
2	5	-23	1763*	695	708
2	5	-22	2169*	1761	614
2	5	-21	1353*	1855	865
2	5	-20	1185*	2261	862
2	5	-19	4403	4828	377
2	5	-18	2786*	3207	545
2	5	-17	2175*	1787	652
2	5	-16	2792*	2023	540
2	5	-15	6373	6460	337
2	5	-14	-1244*	1898	928
2	5	-13	2680*	2808	603
2	5	-12	4346	4552	438
2	5	-11	3113*	4487	518
2	5	-10	3346	3401	438
2	5	-9	5804	5721	320
2	5	-8	5598	5723	302
2	5	-7	7166	7302	247
2	5	-6	5182	5322	279
2	5	-5	11024	9929	207
2	5	-4	3919	3592	311
2	5	-3	13233	12303	196
2	5	-2	3115	2820	364
2	5	-1	12285	11500	193
2	5	0	4549	4849	304
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2	5	2	3151	2821	363
2	5	3	13227	12311	200
2	5	4	3842	3591	313
2	5	5	11379	9927	212
2	5	6	5824	5326	281
2	5	7	6873	7303	256
2	5	8	5430	5719	323
2	5	9	5809	5720	317
2	5	10	3202	3403	470
2	5	11	3829	4491	415
2	5	12	4512	4556	383
2	5	13	594*	2810	1359
2	5	14	2579*	1902	561
2	5	15	6427	6459	304
2	5	16	2686*	2021	518
2	5	17	2190*	1787	548
2	5	18	3088	3204	427
2	5	19	3896	4827	362
2	5	20	1990*	2261	537
2	5	21	1904*	1855	532
2	5	22	2228*	1761	472
2	5	23	615*	[illegible]	1096
2	6	-22	2219*	[illegible]	546
2	6	-21	918*	875	994
2	6	-20	1342*	2190	885
2	6	-19	-2203*	700	665
2	6	-18	2216*	1674	592
2	6	-17	2220*	2713	626
2	6	-16	1885*	2210	656
2	6	-15	3733	3223	442
2	6	-14	8683	7856	278
2	6	-13	5827	5892	327
2	6	-12	2301*	2584	648
2	6	-11	1185*	1816	987
2	6	-10	5787	5184	312
2	6	-9	11070	10848	248
2	6	-8	9639	8757	251
2	6	-7	11121	11078	241
2	6	-6	13671	13680	226
2	6	-5	16169	15870	209
2	6	-4	6924	6901	257
2	6	-3	4153	[illegible]	330
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2	6	2	7357	6713	251
2	6	3	4610	3811	307
2	6	4	6967	6901	278
2	6	5	16426	15878	219
2	6	6	14118	13683	221
2	6	7	11296	11080	236
2	6	8	9713	8760	254
2	6	9	11600	10846	253
2	6	10	5109	5188	379
2	6	11	1663*	1816	810
2	6	12	2449*	2586	611
2	6	13	5546	5891	348
2	6	14	8075	7856	273

h	k	l	Fobs	Fcalc	Sigf
2	6	15	2027*	3223	650
2	6	16	2141*	2211	512
2	6	17	2035*	2712	556
2	6	18	581*	1673	1130
2	6	19	1866*	700	519
2	6	20	2155*	2188	541
2	6	21	1173*	874	739
2	6	22	1439*	1092	703
2	7	-21	-1264*	1370	1011
2	7	-20	-2201*	812	711
2	7	-19	-988*	807	1066
2	7	-18	436*	1680	1357
2	7	-17	1841*	2445	699
2	7	-16	-1536*	547	765
2	7	-15	2166*	2915	629
2	7	-14	2800*	1337	447
2	7	-13	2784*	2432	489
2	7	-12	426*	2624	1464
2	7	-11	9444	10100	262
2	7	-10	5182	4591	358
2	7	-9	4385	4611	412
2	7	-8	8327	8105	271
2	7	-7	8139	8330	267
2	7	-6	9948	9642	250
2	7	-5	4894	4909	348
2	7	-4	10408	9432	246
2	7	-3	4959	4411	347
2	7	-2	4120	3964	345
2	7	-1	390*	959	1325
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2	7	1	-1052*	958	873
2	7	2	3904	3964	392
2	7	3	5218	4416	322
2	7	4	10313	9435	255
2	7	5	4777	4909	363
2	7	6	10065	9644	261
2	7	7	7813	8333	310
2	7	8	8836	8106	269
2	7	9	5074	4609	347
2	7	10	5376	4591	351
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2	7	12	942*	2622	1024
2	7	13	2306*	2433	551
2	7	14	1325*	1336	780
2	7	15	2664*	2915	478
2	7	16	1428*	548	659
2	7	17	2161*	2445	554
2	7	18	1219*	1679	771
2	7	19	-855*	807	1217
2	7	20	-1336*	812	944
2	7	21	-893*	1371	1205
2	8	-20	2386*	1198	566
2	8	-19	2660*	1251	440
2	8	-18	-1932*	904	792
2	8	-17	1286*	1321	778
2	8	-16	1642*	809	664
2	8	-15	2767*	3437	492
2	8	-14	3261	3404	449
2	8	-13	2912*	2590	476
2	8	-12	5593	5352	310
2	8	-11	4706	5653	376
2	8	-10	7618	8038	306
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2	8	-7	2802*	2237	509
2	8	-6	10294	10131	253
2	8	-5	4116	3490	358
2	8	-4	10539	9976	240
2	8	-3	5876	5700	324
2	8	-2	7617	7500	276
2	8	-1	9329	8697	264
2	8	0	10298	9697	254
2	8	1	9126	8698	277
2	8	2	7986	7500	280
2	8	3	5729	5703	348
2	8	4	10643	9978	259
2	8	5	3845	3494	423
2	8	6	10371	10136	268
2	8	7	2982*	2240	505
2	8	8	4527	4391	360
2	8	9	2479*	2501	530
2	8	10	7586	8038	301
2	8	11	4962	5654	350
2	8	12	5504	5352	286
2	8	13	2679*	2585	466
2	8	14	2900*	3402	488
2	8	15	3045	3435	397
2	8	16	-2300*	809	753
2	8	17	1071*	1322	825
2	8	18	-1115*	906	1066
2	8	19	-2546*	1253	669
2	8	20	1608*	1197	695
2	9	-18	-515*	1137	1499
2	9	-17	-876*	316	1182
2	9	-16	-1571*	318	881
2	9	-15	1993*	2400	603
2	9	-14	2097*	2486	529
2	9	-13	1830*	2198	583
2	9	-12	4638	4697	339
2	9	-11	4634	4432	328
2	9	-10	2767	1794	420
2	9	-9	4449	4408	367
2	9	-8	8348	8504	266
2	9	-7	8389	8693	265
2	9	-6	3914	3901	376
2	9	-5	4185	4335	358
2	9	-4	4387	4553	378
2	9	-3	11998	11273	238
2	9	-2	5481	4705	331
2	9	-1	3797	3821	422
2	9	0	1752*	962	684
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2	9	2	4805	4705	394
2	9	3	11770	11274	260
2	9	4	4927	4555	342
2	9	5	3952	4333	415
2	9	6	3484	3898	450
2	9	7	8441	8695	282
2	9	8	8254	8507	278
2	9	9	4693	4410	312
2	9	10	1007*	1795	924
2	9	11	4303	4429	340
2	9	12	4517	4697	332
2	9	13	2821	2196	364
2	9	14	2046*	2487	553
2	9	15	898*	2400	910
2	9	16	2328*	318	423
2	9	17	-1825*	316	704
2	9	18	1369*	1135	713
2	10	-16	1681*	1476	655
2	10	-15	-717*	1441	1436
2	10	-14	-499*	1046	1380
2	10	-13	1460*	1531	605
2	10	-12	-2741*	816	596
2	10	-11	2388*	2198	489
2	10	-10	2025*	3301	601
2	10	-9	3202	3536	405
2	10	-8	4377	3743	312
2	10	-7	3012	1712	364
2	10	-6	980*	1194	915
2	10	-5	7692	7265	261
2	10	-4	2988	2883	422
2	10	-3	1070*	1919	873
2	10	-2	6606	6819	293
2	10	-1	4070	3869	371
2	10	0	5684	5273	319
2	10	1	4497	3869	346
2	10	2	7077	6817	285
2	10	3	2523*	1918	444
2	10	4	2682*	2884	509
2	10	5	7471	7266	269
2	10	6	2302*	1197	475
2	10	7	2328*	1713	513
2	10	8	3399	3745	384
2	10	9	3210	3535	395
2	10	10	3292	3299	389
2	10	11	2141*	2199	543
2	10	12	888*	815	835
2	10	13	1127*	1529	757
2	10	14	1613*	1045	580
2	10	15	-1829*	1441	878
2	10	16	-1364*	1476	1069
2	11	-14	897*	747	983
2	11	-13	1997*	1321	558
2	11	-12	1298*	1701	739
2	11	-11	1388*	1192	604
2	11	-10	1850*	925	495
2	11	-9	1833*	1852	558
2	11	-8	-1183*	295	1015
2	11	-7	3134	3707	392
2	11	-6	389*	1423	1123
2	11	-5	3976	4008	322
2	11	-4	1106*	217	734
2	11	-3	1359*	1441	627
2	11	-2	1803*	1210	544
2	11	-1	2232*	2823	526
2	11	0	1723*	1574	551
2	11	1	3117	2822	386
2	11	2	1253*	1208	745
2	11	3	1857*	1438	511
2	11	4	-1934*	214	682
2	11	5	4325	4009	304
2	11	6	2263*	1424	466
2	11	7	2835*	3706	441
2	11	8	-2318*	296	725
2	11	9	786*	1850	947
2	11	10	-1911*	925	764
2	11	11	-2395*	1190	697
2	11	12	1284*	1701	648
2	11	13	1181*	1320	734
2	11	14	-1375*	747	945
2	12	-10	1843*	1310	590
2	12	-9	1159*	783	720
2	12	-8	1267*	1645	704
2	12	-7	1719*	288	478
2	12	-6	1408*	1744	592

h	k	l	Fobs	Fcalc	Sigf
2	12	-5	-1787*	653	830
2	12	-4	-1208*	1342	1047
2	12	-3	1684*	1063	485
2	12	-2	1393*	1281	641
2	12	-1	1728*	162	493
2	12	0	-690*	250	1195
2	12	1	-1382*	159	943
2	12	2	1778*	1280	509
2	12	3	1506*	1063	579
2	12	4	1699*	1342	578
2	12	5	-1402*	653	923
2	12	6	2082*	1742	493
2	12	7	-1123*	288	1035
2	12	8	1272*	1644	707
2	12	9	-2286*	782	722
2	12	10	1332*	1311	722
2	13	-5	-1163*	54	1111
2	13	-4	2005*	1987	574
2	13	-3	1982*	626	495
2	13	-2	1741*	1774	591
2	13	-1	818*	433	906
2	13	0	-1452*	613	957
2	13	1	-2118*	433	717
2	13	2	2057*	1774	509
2	13	3	-893*	625	1190
2	13	4	2299*	1987	481
2	13	5	0*	54	1821
3	0	1	2786*	2439	466
3	0	2	17112	16766	212
3	0	3	1712*	1351	811
3	0	4	6004	4329	323
3	0	5	5199	5834	373
3	0	6	5028	5264	407
3	0	7	2841*	1846	635
3	0	8	5610	4954	393
3	0	9	11160	10653	292
3	0	10	5351	4404	450
3	0	11	10268	10842	312
3	0	12	9717	9839	344
3	0	13	1937*	1930	943
3	0	14	-1182*	310	957
3	0	15	8175	9522	341
3	0	16	6632	6752	367
3	0	17	2349*	2314	670
3	0	18	3817	4492	414
3	0	19	781*	1086	1013
3	0	20	1530*	124	740
3	0	21	2124*	1370	543
3	0	22	-789*	1538	1172
3	0	23	2321*	2325	582
3	1	-23	2143*	76	657
3	1	-22	-2031*	1235	795
3	1	-21	-1644*	1491	919
3	1	-20	0*	1181	1906
3	1	-19	2101*	2014	652
3	1	-18	2938*	2989	556
3	1	-17	2940*	2732	623
3	1	-16	-879*	1716	1103
3	1	-15	490*	1189	1638
3	1	-14	10558	9939	325
3	1	-13	11626	12909	325
3	1	-12	10463	10243	341
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3	1	-10	1738*	733	887
3	1	-9	7447	7753	337
3	1	-8	10952	11352	270
3	1	-7	13290	13650	236
3	1	-6	8021	7742	267
3	1	-5	6629	6234	273
3	1	-4	5867	6020	314
3	1	-3	5699	5431	316
3	1	-2	5304	5069	339
3	1	-1	9451	9253	242
3	1	0	774*	1450	1061
3	1	1	8879	9258	226
3	1	2	4921	5073	318
3	1	3	5585	5427	276
3	1	4	6448	6021	274
3	1	5	6812	6231	287
3	1	6	9064	7741	270
3	1	7	13898	13646	251
3	1	8	11273	11351	270
3	1	9	7395	7749	343
3	1	10	1238*	735	1094
3	1	11	3613*	3601	566
3	1	12	9946	10244	317
3	1	13	11341	12913	295
3	1	14	10831	9936	284
3	1	15	1686*	1187	802
3	1	16	-1319*	1716	844
3	1	17	1961*	2733	744
3	1	18	2981*	2988	519
3	1	19	-472*	2015	1510
3	1	20	1316*	1180	714
3	1	21	-1214*	1493	1019
3	1	22	601*	1233	1149
3	1	23	2374*	76	486
3	2	-22	0*	573	1823
3	2	-21	1417*	1149	934
3	2	-20	1812*	699	696
3	2	-19	1558*	2940	893
3	2	-18	3968	2979	430
3	2	-17	2297*	3134	666
3	2	-16	7097	7401	375
3	2	-15	5941	5625	453
3	2	-14	4060	4591	508
3	2	-13	3233*	3695	636
3	2	-12	7398	6255	356
3	2	-11	6216	6660	386
3	2	-10	-1024*	2715	994
3	2	-9	7215	7580	321
3	2	-8	1802*	2525	754
3	2	-7	6013	6507	313
3	2	-6	3295	2838	457
3	2	-5	8264	8015	267
3	2	-4	8415	8279	278
3	2	-3	2089*	2744	674
3	2	-2	7506	6956	287
3	2	-1	7117	6368	278
3	2	0	5381	5178	308
3	2	1	6455	6375	278
3	2	2	7045	6953	272
3	2	3	2247*	2743	556
3	2	4	8342	8280	238
3	2	5	7497	8015	302
3	2	6	1859*	2838	815
3	2	7	6367	6502	332
3	2	8	1301*	2528	946
3	2	9	7946	7575	305
3	2	10	-1340*	2714	904
3	2	11	6516	6660	357
3	2	12	7254	6252	332
3	2	13	2251*	3697	751
3	2	14	4135	4589	474
3	2	15	5650	5629	393
3	2	16	6737	7402	332
3	2	17	1241*	3135	880
3	2	18	3506	2978	416
3	2	19	2583*	2938	532
3	2	20	1683*	697	668
3	2	21	-1411*	1150	962
3	2	22	-510*	574	1426
3	3	-22	1594*	462	864
3	3	-21	3781	2698	391
3	3	-20	1558*	1059	812
3	3	-19	0*	336	1883
3	3	-18	1556*	2009	900
3	3	-17	2350*	2630	572
3	3	-16	669*	2656	1385
3	3	-15	3894	4054	474
3	3	-14	8117	8415	360
3	3	-13	6568	6570	331
3	3	-12	2310*	1559	714
3	3	-11	4264	4514	451
3	3	-10	3825	2730	474
3	3	-9	4250	5818	467
3	3	-8	1226*	1899	951
3	3	-7	12204	12210	242
3	3	-6	10761	11000	253
3	3	-5	2208*	2124	651
3	3	-4	4758	4328	338
3	3	-3	15945	14399	229
3	3	-2	9604	9569	263
3	3	-1	8576	8429	283
3	3	0	16588	15680	223
3	3	1	8754	8425	270
3	3	2	8998	9574	251
3	3	3	14678	14405	220
3	3	4	3419	4330	466
3	3	5	2178*	2127	654
3	3	6	10868	10996	251
3	3	7	12076	12208	251
3	3	8	1485*	1899	925
3	3	9	5332	5815	373
3	3	10	3803	2729	477
3	3	11	3920	4514	484
3	3	12	3044*	1559	497
3	3	13	5748	6572	388
3	3	14	7946	8417	337
3	3	15	3630	4054	444
3	3	16	2937*	2655	496
3	3	17	2354*	2633	579
3	3	18	1293*	2008	861
3	3	19	2255*	337	521
3	3	20	1276*	1058	762
3	3	21	2203*	2697	562
3	3	22	-1030*	464	1249
3	4	-21	3119*	1481	512
3	4	-20	2640*	1386	480
3	4	-19	1473*	2915	951
3	4	-18	1036*	1261	1039
3	4	-17	463*	2135	1350
3	4	-16	3680	3410	420
3	4	-15	6228	7097	380
3	4	-14	1659*	1819	854
3	4	-13	5504	6040	395

h	k	l	Fobs	Fcalc	Sigf
3	4	-12	4939	6265	432
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3	4	-10	2451*	3209	653
3	4	-9	3612	4613	534
3	4	-8	1677*	2199	844
3	4	-7	2624*	3250	628
3	4	-6	4810	4250	372
3	4	-5	3613	2278	430
3	4	-4	4981	5580	402
3	4	-3	8865	8235	288
3	4	-2	1702*	1655	810
3	4	-1	10259	10860	285
3	4	0	4987	5081	405
3	4	1	10175	10865	273
3	4	2	2126*	1659	649
3	4	3	8235	8236	299
3	4	4	4364	5584	411
3	4	5	3219	2277	472
3	4	6	4436	4251	384
3	4	7	4722	3251	379
3	4	8	2876*	2194	555
3	4	9	5190	4616	368
3	4	10	1838*	3211	834
3	4	11	2879*	1436	574
3	4	12	5743	6264	361
3	4	13	5268	6039	421
3	4	14	3419	1819	412
3	4	15	6201	7095	343
3	4	16	3802	3407	398
3	4	17	1149*	2134	826
3	4	18	1550*	1260	730
3	4	19	2710*	2916	463
3	4	20	1560*	1385	675
3	4	21	1182*	1481	839
3	5	-21	-2436*	435	722
3	5	-20	1374*	1709	933
3	5	-19	2145*	1699	587
3	5	-18	-1461*	572	925
3	5	-17	2847*	3886	550
3	5	-16	2180*	2971	660
3	5	-15	2976*	4427	606
3	5	-14	3415	3330	444
3	5	-13	7776	7626	304
3	5	-12	3759	3452	407
3	5	-11	8723	9385	301
3	5	-10	2313*	3446	691
3	5	-9	4877	4765	412
3	5	-8	4378	3799	416
3	5	-7	4867	4887	396
3	5	-6	7709	7481	327
3	5	-5	425*	3077	1606
3	5	-4	7572	7820	333
3	5	-3	6635	6820	347
3	5	-2	3387*	2201	534
3	5	-1	5376	5288	406
3	5	0	2289*	2156	709
3	5	1	5454	5289	378
3	5	2	3319*	2198	559
3	5	3	6260	6822	349
3	5	4	7796	7818	301
3	5	5	3119*	3076	518
3	5	6	7851	7483	328
3	5	7	4930	4890	407
3	5	8	3771	3798	481
3	5	9	5366	4765	379
3	5	10	3361*	3448	536
3	5	11	8219	9386	315
3	5	12	1769*	3453	832
3	5	13	7377	7623	309
3	5	14	2455*	3326	606
3	5	15	3640	4425	437
3	5	16	1894*	2970	652
3	5	17	2926*	3884	481
3	5	18	-688*	573	1219
3	5	19	-2169*	1699	776
3	5	20	1671*	1710	641
3	5	21	-1558*	431	931
3	6	-20	-1373*	733	1020
3	6	-19	-1016*	341	990
3	6	-18	2695*	1004	462
3	6	-17	-2442*	257	642
3	6	-16	447*	1510	1361
3	6	-15	1090*	1808	992
3	6	-14	-1843*	873	704
3	6	-13	2970*	3393	492
3	6	-12	4141	4620	437
3	6	-11	-1448*	2538	898
3	6	-10	1580*	269	736
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3	6	-3	3418*	2875	561
3	6	-2	-683*	1208	1233
3	6	-1	3617	2523	479
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3	6	1	-1362*	2520	860
3	6	2	1381*	1207	954
3	6	3	2956*	2877	627
3	6	4	2919*	1719	542
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3	6	6	2386*	2225	677
3	6	7	6065	6104	375
3	6	8	8249	7261	283
3	6	9	1242*	1327	977
3	6	10	1918*	270	675
3	6	11	1245*	2538	1009
3	6	12	4216	4618	388
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3	6	14	-921*	875	1018
3	6	15	1224*	1804	850
3	6	16	1554*	1508	740
3	6	17	-976*	257	1079
3	6	18	1380*	1005	738
3	6	19	-1137*	339	1048
3	6	20	1423*	733	850
3	7	-18	1515*	492	788
3	7	-17	1714*	753	614
3	7	-16	-491*	1656	1482
3	7	-15	761*	390	1025
3	7	-14	3322	3515	411
3	7	-13	2130*	2512	628
3	7	-12	-2341*	1714	641
3	7	-11	3528	3839	436
3	7	-10	3935	3515	413
3	7	-9	5130	6279	368
3	7	-8	5978	6155	333
3	7	-7	4305	4546	406
3	7	-6	-733*	1378	1256
3	7	-5	5245	4904	377
3	7	-4	8935	9573	300
3	7	-3	4917	4624	408
3	7	-2	770*	2685	1375
3	7	-1	6486	6222	363
3	7	0	3594	4291	534
3	7	1	6700	6220	362
3	7	2	1408*	2684	1018
3	7	3	4618	4624	425
3	7	4	9281	9575	301
3	7	5	5651	4904	347
3	7	6	2296*	1376	581
3	7	7	3870	4548	484
3	7	8	5857	6155	361
3	7	9	5642	6280	319
3	7	10	3664	3513	423
3	7	11	3623	3839	419
3	7	12	2456*	1714	513
3	7	13	2159*	2513	590
3	7	14	3190	3517	412
3	7	15	2016*	391	607
3	7	16	2328*	1658	548
3	7	17	2199*	753	536
3	7	18	2086*	491	589
3	8	-17	839*	602	1168
3	8	-16	1026*	2212	1040
3	8	-15	1773*	1114	628
3	8	-14	2944*	2524	463
3	8	-13	1357*	637	763
3	8	-12	3865	4887	409
3	8	-11	-1147*	270	995
3	8	-10	1479*	1838	744
3	8	-9	1484*	2676	778
3	8	-8	8141	8504	288
3	8	-7	1885*	875	663
3	8	-6	5361	6287	358
3	8	-5	4416	3210	374
3	8	-4	6400	6472	348
3	8	-3	1821*	2503	850
3	8	-2	10704	11058	290
3	8	-1	8492	8444	316
3	8	0	3804	4077	521
3	8	1	8028	8445	307
3	8	2	11379	11059	278
3	8	3	2176*	2504	741
3	8	4	6961	6471	320
3	8	5	3183	3207	486
3	8	6	5258	6286	354
3	8	7	1158*	875	937
3	8	8	8983	8501	264
3	8	9	2033*	2678	590
3	8	10	610*	1837	1156
3	8	11	2013*	269	577
3	8	12	4058	4888	411
3	8	13	855*	636	937
3	8	14	2273*	2524	518
3	8	15	1306*	1115	750
3	8	16	1611*	2214	767
3	8	17	0*	602	1876
3	9	-15	1880*	897	666
3	9	-14	777*	1274	1034
3	9	-13	-1500*	1453	940
3	9	-12	-1304*	962	980
3	9	-11	-842*	1735	1256
3	9	-10	2755*	3154	490

h	k	l	Fobs	Fcalc	Sigf
3	9	-9	-2015*	1826	757
3	9	-8	421*	914	1204
3	9	-7	2115*	2915	626
3	9	-6	5816	5706	288
3	9	-5	3314	3625	472
3	9	-4	4104	4630	392
3	9	-3	1297*	1516	872
3	9	-2	4513	5377	421
3	9	-1	-1493*	1055	919
3	9	0	8418	8038	273
3	9	1	1310*	1055	880
3	9	2	4598	5378	411
3	9	3	1796*	1518	707
3	9	4	4277	4629	394
3	9	5	3488	3625	420
3	9	6	5259	5705	332
3	9	7	2845*	2914	520
3	9	8	-1050*	915	1098
3	9	9	2481*	1825	510
3	9	10	2247*	3155	604
3	9	11	-486*	1734	1522
3	9	12	1210*	962	763
3	9	13	970*	1453	922
3	9	14	-1435*	1276	934
3	9	15	1132*	898	893
3	10	-13	938*	282	1016
3	10	-12	-511*	545	1430
3	10	-11	2881	1587	386
3	10	-10	1203*	893	769
3	10	-9	-1484*	1752	969
3	10	-8	723*	2452	1058
3	10	-7	2243*	2046	575
3	10	-6	-681*	1620	1384
3	10	-5	2471*	2507	490
3	10	-4	-951*	965	1183
3	10	-3	-669*	1740	1341
3	10	-2	1521*	1263	709
3	10	-1	2278*	1237	490
3	10	0	1798*	675	551
3	10	1	1039*	1239	918
3	10	2	1587*	1263	726
3	10	3	2321*	1741	543
3	10	4	-1345*	966	976
3	10	5	2500*	2508	478
3	10	6	731*	1623	1050
3	10	7	1194*	2046	887
3	10	8	2538*	2452	480
3	10	9	1473*	1752	749
3	10	10	430*	893	1204
3	10	11	1749*	1586	629
3	10	12	-1916*	546	762
3	10	13	-1372*	280	982
3	11	-10	-3530*	925	560
3	11	-9	-1785*	634	778
3	11	-8	2693*	1138	468
3	11	-7	2611*	1188	403
3	11	-6	949*	1078	942
3	11	-5	1736*	1186	558
3	11	-4	2220*	1828	545
3	11	-3	2331*	1861	494
3	11	-2	1674*	964	657
3	11	-1	-2093*	886	771
3	11	0	-1102*	332	1065
3	11	1	1781*	886	588
3	11	2	728*	965	993
3	11	3	1738*	1862	577
3	11	4	1745*	1829	621
3	11	5	-1581*	1185	897
3	11	6	2058*	1077	522
3	11	7	2418*	1187	470
3	11	8	1531*	1138	687
3	11	9	1359*	633	723
3	11	10	1987*	925	589
3	12	-4	2856*	2315	466
3	12	-3	452*	760	1292
3	12	-2	2006*	1054	615
3	12	-1	632*	1020	1187
3	12	0	2929*	2639	453
3	12	1	2003*	1020	562
3	12	2	-730*	1055	1390
3	12	3	-1554*	760	917
3	12	4	2008*	2316	668
4	0	0	-686*	3938	1361
4	0	1	2980*	2082	667
4	0	2	1452*	931	957
4	0	3	7654	5884	405
4	0	4	-1294*	339	1308
4	0	5	5161	3994	432
4	0	6	1035*	134	1372
4	0	7	-1400*	2006	1190
4	0	8	-663*	1651	1516
4	0	9	1502*	1962	1063
4	0	10	4960	5612	513
4	0	11	4937	4048	482
4	0	12	4042	4136	544
4	0	13	150*	3289	1950
4	0	14	1876*	1898	829
4	0	15	1996*	473	673
4	0	16	-900*	292	1180
4	0	17	-2111*	458	758
4	0	18	-1336*	608	1022
4	0	19	932*	1104	1144
4	1	-19	1611*	897	873
4	1	-18	0*	790	1950
4	1	-17	-1390*	1972	1028
4	1	-16	-1738*	521	852
4	1	-15	2734*	2331	612
4	1	-14	4982	5476	450
4	1	-13	2601*	2155	727
4	1	-12	6311	5115	363
4	1	-11	1894*	2307	904
4	1	-10	8907	9761	328
4	1	-9	4037	3153	489
4	1	-8	5802	5467	367
4	1	-7	2505*	3259	686
4	1	-6	6666	7227	367
4	1	-5	5329	6353	433
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4	1	-3	465*	3555	1857
4	1	-2	2785*	2742	770
4	1	-1	4889	5093	463
4	1	0	1351*	3091	990
4	1	1	4673	5094	435
4	1	2	2982*	2743	648
4	1	3	3941	3556	487
4	1	4	2617*	2997	769
4	1	5	4883	6349	505
4	1	6	7441	7227	397
4	1	7	2393*	3260	814
4	1	8	6197	5466	395
4	1	9	3369*	3153	633
4	1	10	8982	9765	346
4	1	11	2422*	2308	700
4	1	12	4136	5115	541
4	1	13	2873*	2154	637
4	1	14	4339	5477	483
4	1	15	2268*	2331	640
4	1	16	-1078*	520	1147
4	1	17	1093*	1971	917
4	1	18	-1586*	789	959
4	1	19	1906*	896	633
4	2	-19	-1543*	720	1008
4	2	-18	1775*	1090	854
4	2	-17	1919*	2585	736
4	2	-16	1570*	2942	856
4	2	-15	2302*	1033	651
4	2	-14	1402*	2990	959
4	2	-13	2582*	3946	648
4	2	-12	3245*	4545	527
4	2	-11	5141	4793	375
4	2	-10	5385	5947	376
4	2	-9	1243*	3005	1014
4	2	-8	6628	7174	350
4	2	-7	3916	4659	508
4	2	-6	5234	4646	390
4	2	-5	3451*	3355	590
4	2	-4	934*	2106	1396
4	2	-3	6931	6600	403
4	2	-2	3024*	3027	733
4	2	-1	6416	6934	396
4	2	0	1974*	879	859
4	2	1	6798	6932	329
4	2	2	3013*	3027	610
4	2	3	5798	6598	365
4	2	4	2003*	2103	779
4	2	5	-711*	3355	1314
4	2	6	4257	4644	532
4	2	7	4799	4659	436
4	2	8	6141	7173	410
4	2	9	-1218*	3005	1037
4	2	10	5708	5945	346
4	2	11	4434	4791	461
4	2	12	3677	4546	503
4	2	13	2602*	3945	641
4	2	14	1987*	2990	755
4	2	15	1498*	1035	850
4	2	16	1420*	2941	808
4	2	17	-494*	2584	1536
4	2	18	-1595*	1088	895
4	2	19	474*	722	1313
4	3	-19	0*	1573	2032
4	3	-18	2432*	1904	640
4	3	-17	2290*	1171	616
4	3	-16	-2138*	1773	742
4	3	-15	-2724*	450	619
4	3	-14	2450*	323	519
4	3	-13	2210*	3193	639
4	3	-12	2050*	3263	722
4	3	-11	-1855*	1211	795
4	3	-10	3973	4886	460
4	3	-9	5626	5716	329
4	3	-8	-1219*	1955	963
4	3	-7	-851*	1248	1193
4	3	-6	4271	4187	470
4	3	-5	2896*	2023	647
4	3	-4	815*	296	1417

h	k	l	Fobs	Fcalc	Sigf
4	3	-3	5975	5620	459
4	3	-2	5304	5390	424
4	3	-1	5525	4588	438
4	3	0	-408*	929	1491
4	3	1	4509	4588	490
4	3	2	4109	5388	505
4	3	3	6393	5619	356
4	3	4	-1374*	297	963
4	3	5	1734*	2022	850
4	3	6	4156	4185	443
4	3	7	-2213*	1249	687
4	3	8	-430*	1953	1517
4	3	9	4311	5719	489
4	3	10	4545	4885	411
4	3	11	1018*	1210	1106
4	3	12	3434	3262	451
4	3	13	2076*	3194	732
4	3	14	-2219*	323	743
4	3	15	-1597*	449	943
4	3	16	1622*	1771	842
4	3	17	1203*	1173	907
4	3	18	2090*	1904	649
4	3	19	2251*	1573	645
4	4	-18	-2128*	2314	789
4	4	-17	2412*	1352	596
4	4	-16	2372*	811	560
4	4	-15	2911*	2096	475
4	4	-14	1268*	815	880
4	4	-13	628*	2430	1309
4	4	-12	3276	3414	472
4	4	-11	-647*	1977	1380
4	4	-10	4731	4870	373
4	4	-9	-995*	1706	1109
4	4	-8	1790*	1403	756
4	4	-7	1570*	2190	831
4	4	-6	2642*	2118	618
4	4	-5	3818	3557	527
4	4	-4	-1197*	2381	999
4	4	-3	-594*	2117	1379
4	4	-2	2913*	2746	684
4	4	-1	3888	4572	534
4	4	0	4521	5072	504
4	4	1	3399*	4571	618
4	4	2	1416*	2746	1078
4	4	3	2029*	2118	773
4	4	4	1647*	2381	883
4	4	5	2948*	3558	607
4	4	6	2854*	2118	562
4	4	7	1595*	2189	806
4	4	8	-621*	1401	1224
4	4	9	-444*	1707	1431
4	4	10	4501	4870	417
4	4	11	1793*	1973	735
4	4	12	2455*	3414	623
4	4	13	1614*	2432	785
4	4	14	2237*	815	568
4	4	15	2153*	2098	602
4	4	16	-497*	811	1433
4	4	17	930*	1353	1120
4	4	18	2061*	2313	750
4	5	-17	-728*	1324	1276
4	5	-16	2461*	753	601
4	5	-15	-704*	748	1314
4	5	-14	-2545*	1488	666
4	5	-13	2163*	3932	663
4	5	-12	-671*	1533	1311
4	5	-11	0*	3187	1967
4	5	-10	3324	4015	478
4	5	-9	4818	5919	378
4	5	-8	1186*	1249	977
4	5	-7	1111*	2522	1072
4	5	-6	2871*	4612	622
4	5	-5	2673*	2249	631
4	5	-4	2395*	1218	660
4	5	-3	-431*	743	1407
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4	5	2	-1490*	2155	873
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4	5	7	2032*	2522	734
4	5	8	-1102*	1249	1055
4	5	9	5228	5917	365
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4	5	12	-949*	1533	1190
4	5	13	1665*	3931	799
4	5	14	776*	1488	1145
4	5	15	642*	747	1239
4	5	16	-716*	755	1283
4	5	17	1087*	1325	1034
4	6	-16	996*	1024	1104
4	6	-15	2261*	1020	546
4	6	-14	1114*	587	965
4	6	-13	1938*	1345	620
4	6	-12	-1375*	2366	979
4	6	-11	978*	2529	1028
4	6	-10	1807*	2024	760
4	6	-9	624*	858	1193
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4	6	-7	2737*	3697	601
4	6	-6	-1014*	2806	1114
4	6	-5	2108*	1083	612
4	6	-4	2023*	1178	704
4	6	-3	5600	6564	408
4	6	-2	3469	2043	495
4	6	-1	2472*	2899	640
4	6	0	-988*	441	1060
4	6	1	2401*	2899	690
4	6	2	3142*	2042	502
4	6	3	5730	6565	376
4	6	4	1425*	1175	889
4	6	5	1097*	1083	969
4	6	6	2226*	~~2806~~	~~671~~
4	6	7	3682	3697	466
4	6	8	2688*	3700	559
4	6	9	2115*	857	528
4	6	10	1650*	2021	813
4	6	11	2163*	2529	632
4	6	12	1255*	2363	907
4	6	13	-2206*	1345	722
4	6	14	-1325*	587	1007
4	6	15	-2098*	1018	804
4	6	16	1392*	1025	840
4	7	-14	-726*	332	1315
4	7	-13	-2429*	462	610
4	7	-12	-2497*	1512	657
4	7	-11	1972*	1605	612
4	7	-10	1160*	412	903
4	7	-9	2595*	3069	555
4	7	-8	623*	1982	1272
4	7	-7	2589*	2286	562
4	7	-6	-1238*	2322	1085
4	7	-5	1750*	2597	822
4	7	-4	3019*	3905	566
4	7	-3	2378*	1897	647
4	7	-2	2514*	4637	677
4	7	-1	-3136*	813	553
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4	7	1	-1446*	812	900
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4	7	3	2512*	1898	552
4	7	4	2973*	3904	558
4	7	5	2921*	2599	519
4	7	6	2215*	2321	577
4	7	7	2993*	2286	460
4	7	8	2112*	1982	646
4	7	9	2568*	3068	522
4	7	10	-1192*	411	1055
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4	7	12	1196*	1511	921
4	7	13	1389*	462	840
4	7	14	480*	332	1359
4	8	-12	2592*	2338	586
4	8	-11	1448*	1800	785
4	8	-10	2872*	3319	498
4	8	-9	1983*	1019	566
4	8	-8	2860*	2282	451
4	8	-7	624*	501	1172
4	8	-6	1770*	3163	802
4	8	-5	629*	718	1283
4	8	-4	3487	4537	486
4	8	-3	2102*	2056	632
4	8	-2	1556*	1120	783
4	8	-1	-1253*	1511	1074
4	8	0	6652	7838	332
4	8	1	2616*	1511	562
4	8	2	0*	1119	1946
4	8	3	1478*	2056	806
4	8	4	3075*	4535	570
4	8	5	-1520*	717	946
4	8	6	1874*	3162	770
4	8	7	765*	501	1043
4	8	8	1174*	2282	913
4	8	9	632*	1019	1220
4	8	10	2484*	3320	541
4	8	11	-1015*	1799	1231
4	8	12	830*	2339	1214
4	9	-10	838*	622	1101
4	9	-9	1406*	1767	890
4	9	-8	1655*	1084	706
4	9	-7	2396*	2014	531
4	9	-6	2200*	2993	594
4	9	-5	1265*	805	859
4	9	-4	1997*	2431	658
4	9	-3	1670*	2178	748
4	9	-2	4929	5235	370
4	9	-1	-2143*	1462	847
4	9	0	3865	4242	425
4	9	1	1995*	1461	635
4	9	2	4804	5234	330
4	9	3	1545*	2178	818

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 h  k  l    Fobs  Fcalc  Sigf     h  k  l    Fobs  Fcalc  Sigf     h  k  l    Fobs  Fcalc  Sigf     h  k  l    Fobs  Fcalc  Sigf
 -  -  -    ----  -----  ----     -  -  -    ----  -----  ----     -  -  -    ----  -----  ----     -  -  -    ----  -----  ----

 4  9  4   2643*   2430   531     5  1  1   2549*   3069   561     5  3 -7   1484*   3096   889     5  5 -8   1899*   2048   725
 4  9  5   1487*    806   727     5  1  2  -1216*   2816  1154     5  3 -6   2590*   2299   616     5  5 -7   1221*   1329   930
 4  9  6   2592*   2993   559     5  1  3  -1901*   2175   828     5  3 -5   2137*   1427   772     5  5 -6   1135*   1963  1078
 4  9  7  -1336*   2014  1047     5  1  4  -1036*   2518  1234     5  3 -4   2969*   4122   625     5  5 -5  -1300*   1266  1096
 4  9  8  -1527*   1084   901     5  1  5   3838    4063   465     5  3 -3   1806*   2144   812     5  5 -4   1865*   1891   765
 4  9  9  -1258*   1768  1134     5  1  6   -663*   1692  1459     5  3 -2   -468*   1675  1573     5  5 -3   1741*   1440   836
 4  9 10   2352*    623   587     5  1  7   1796*   2700   898     5  3 -1  -2561*    182   701     5  5 -2   1386*   1209   940
 4 10 -6  -2080*    897   795     5  1  8   2190*   2135   767     5  3  0   3446    3455   455     5  5 -1   1210*    714  1054
 4 10 -5   2292*    635   572     5  1  9   3316*   3177   571     5  3  1   1994*    183   658     5  5  0  -1875*   1499   882
 4 10 -4   2871*   1815   482     5  1 10  -2441*    723   728     5  3  2   2056*   1674   630     5  5  1  -2518*    714   724
 4 10 -3   1930*   1079   678     5  1 11   2460*    461   586     5  3  3  -1243*   2144  1073     5  5  2    881*   1209  1089
 4 10 -2      0*    916  1947     5  1 12   2343*   2058   632     5  3  4   2877*   4121   555     5  5  3  -1377*   1439  1027
 4 10 -1   -721*   1675  1386     5  1 13  -1342*    775  1103     5  3  5    423*   1427  1407     5  5  4      0*   1892  2015
 4 10  0  -1530*    773   969     5  1 14  -3493*    246   596     5  3  6   3318    2299   431     5  5  5   -694*   1265  1334
 4 10  1   1315*   1674   960     5  2-14      0*   2004  1972     5  3  7    614*   3096  1354     5  5  6   1239*   1963   929
 4 10  2    933*    916  1092     5  2-13  -2749*   1132   686     5  3  8   2157*   2809   649     5  5  7  -2729*   1328   680
 4 10  3   1757*   1078   715     5  2-12   1896*     37   675     5  3  9   1788*   1870   777     5  5  8  -2071*   2048   888
 4 10  4  -1029*   1816  1188     5  2-11  -1989*   1960   805     5  3 10   -859*   1612  1344     5  5  9   1662*   1442   800
 4 10  5   1361*    635   846     5  2-10   2158*   2332   618     5  3 11   2670*    686   522     5  5 10  -1699*   1551   986
 4 10  6   2549*    898   591     5  2 -9  -2003*   1216   837     5  3 12    676*   1047  1257     5  5 11  -1637*   1122   991
 5  0  1   1279*   1962   942     5  2 -8    426*   1868  1363     5  3 13  -1152*   1109  1088     5  6 -9   -732*    627  1405
 5  0  2   2615*   4615   622     5  2 -7   1517*   4306   908     5  4-12  -2525*    763   698     5  6 -8  -2053*    196   785
 5  0  3   2724*   3473   654     5  2 -6   3270*   4989   578     5  4-11  -2333*    458   763     5  6 -7   1264*   1453   963
 5  0  4   3020*   3749   653     5  2 -5   2238*    750   705     5  4-10   1266*   1026   897     5  6 -6      0*   2148  1952
 5  0  5   1406*   1248  1062     5  2 -4   3769    3113   509     5  4 -9   1179*    909  1004     5  6 -5   3209    1606   429
 5  0  6   -398*   2814  1736     5  2 -3      0*   3461  2016     5  4 -8  -2093*    840   787     5  6 -4      0*   1227  2017
 5  0  7   3662    3529   508     5  2 -2   2454*   2839   628     5  4 -7   2128*   2003   647     5  6 -3  -1317*    935  1053
 5  0  8   2189*   3027   773     5  2 -1   1553*   2311   846     5  4 -6  -2059*   1945   853     5  6 -2   1144*   1483  1021
 5  0  9   1763*   1886   847     5  2  0   2706*   1532   524     5  4 -5      0*    744  2027     5  6 -1  -1487*   1577   991
 5  0 10   1634*    893   901     5  2  1   2327*   2311   543     5  4 -4  -1356*   1033  1063     5  6  0  -2324*   1633   743
 5  0 11   2665*   1250   661     5  2  2   2057*   2839   626     5  4 -3   1976*   3295   838     5  6  1   -495*   1578  1584
 5  0 12   1135*    874  1109     5  2  3   3275    3460   439     5  4 -2   2304*   1784   730     5  6  2   1631*   1484   768
 5  0 13    784*    202  1233     5  2  4   1036*   3113  1103     5  4 -1  -1062*   2207  1210     5  6  3  -1494*    935   995
 5  0 14   2034*     39   824     5  2  5  -1327*    750  1079     5  4  0   2179*    776   623     5  6  4  -1224*   1227  1104
 5  1-14   1822*    247   868     5  2  6   3963    4989   450     5  4  1   2797*   2208   480     5  6  5   2556*   1606   566
 5  1-13   1073*    775  1076     5  2  7   3203*   4305   507     5  4  2    746*   1784  1231     5  6  6   1881*   2148   726
 5  1-12  -2453*   2060   759     5  2  8   1683*   1867   793     5  4  3   2298*   3293   652     5  6  7  -1440*   1453  1035
 5  1-11   1595*    462   751     5  2  9   1115*   1216  1066     5  4  4   1648*   1033   761     5  6  8  -2177*    196   710
 5  1-10   3229     723   420     5  2 10  -1474*   2332  1051     5  4  5  -3050*    745   598     5  6  9  -1937*    627   916
 5  1 -9   2284*   3176   590     5  2 11  -1989*   1960   869     5  4  6   2646*   1943   528     5  7 -6   2076*   1159   748
 5  1 -8   2067*   2133   612     5  2 12   1345*     37   811     5  4  7   1988*   2000   669     5  7 -5   1790*   1098   795
 5  1 -7   1837*   2700   710     5  2 13   1691*   1133   831     5  4  8    622*    840  1211     5  7 -4   2407*    956   561
 5  1 -6   1652*   1693   801     5  2 14   1343*   2003  1116     5  4  9    896*    908  1079     5  7 -3  -1351*    885  1027
 5  1 -5   3314*   4064   596     5  3-13   1570*   1109   865     5  4 10  -1125*   1026  1217     5  7 -2    684*   1306  1308
 5  1 -4    666*   2518  1451     5  3-12   1107*   1047   929     5  4 11    945*    458  1083     5  7 -1   2495*   1214   594
 5  1 -3  -2396*   2176   760     5  3-11  -1945*    687   842     5  4 12   1474*    763   953     5  7  0   2658*    847   577
 5  1 -2   3784    2816   417     5  3-10    612*   1612  1220     5  5-11  -2429*   1121   799     5  7  1   1344*   1213   953
 5  1 -1   1466*   3071   817     5  3 -9    749*   1871  1125     5  5-10  -1448*   1551   966     5  7  2   -720*   1306  1383
 5  1  0  -2292*   1255   763     5  3 -8   1314*   2810   883     5  5 -9    463*   1443  1461     5  7  3  -1021*    886  1227

 5  7  4   1433*    956   866     5  7  5   2316*   1098   597     5  7  6  -2259*   1159   757     6  0  0   3157*   3255   501
 6  0  1   2735*   1011   575     6  0  2   1367*   1564  1010     6  1 -1  -1726*    929  1028     6  1  0  -2268*    362   910
 6  1  1  -2654*    929   797
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